

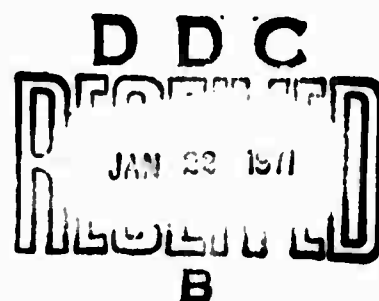
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NORTHWESTERN UNIVERSITY

MATERIALS RESEARCH CENTER

ANNUAL TECHNICAL REPORT

1969-70

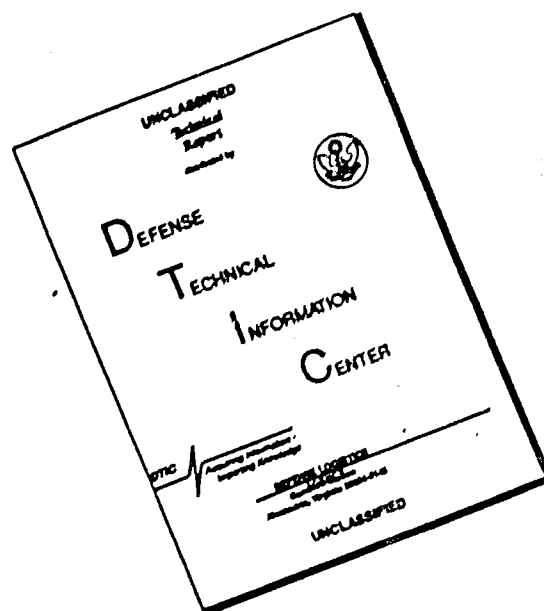


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ELEVENTH ANNUAL REPORT

RESEARCH SUPPORTED BY THE

ADVANCED RESEARCH PROJECTS AGENCY

DEPARTMENT OF DEFENSE

CONTRACTS SD-67 and DAHC 15 67 C0213

REPORT PERIOD

1 October 1969 to 30 September 1970

MATERIALS RESEARCH CENTER
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS 60201

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INTRODUCTION

The Materials Research Center (MRC) at Northwestern University was founded in 1960, under the auspices of the Advanced Research Projects Agency (ARPA) of the Department of Defense, for the purpose of conducting an expanded and coordinated interdisciplinary program of basic research and graduate education in the materials science area. The MRC is an association of professors, their graduate students and postdoctoral research associates interested in various facets of materials science.

During the 12-month period covered by this Report, there were 43 professors, 22 postdoctoral research associates and 176 graduate students associated with the MRC, mainly from six academic departments within two major colleges of the University. In addition, various other professors and graduate students from the Medical and Dental Schools and the Departments of Biology and Geology made use of the major research equipment and services which are provided by the seventeen Central Facility Laboratories operated by the MRC.

The Scientific Advisory Committee composed of

D. H. Whitmore, Director of MRC and Professor of Materials Science

J. Dundurs, Professor of Civil Engineering

M. Epstein, Associate Professor of Electrical Engineering

A. W. Ewald, Professor of Physics

J. E. Hilliard, Professor of Materials Science

F. E. Stafford, Associate Professor of Chemistry

is the working faculty committee of the MRC which makes decisions regarding funding of individual research projects, determines future directions for its scientific and technological activities and establishes the day-to-day operating policies of the MRC. The MRC Director is responsible to the Administrative Committee comprised of all interested Departmental Chairmen, the Deans of the College of Arts and Sciences and the Technological Institute and chaired by the Provost of the University. This latter committee is concerned mainly with establishing broad-range policies for the Center.

All faculty participants in the MRC receive some direct support of their research programs with funds derived from the ARPA Contract. Other funding agencies provide financial support for some of the research reported on here; sources of support other than ARPA are indicated, where applicable, on the individual project reports. Even in these latter cases, ARPA support plays a significant role in providing the MRC central facilities and/or space essential to the achievement of the research objectives of the project.

This Annual Report is a condensed account of the total materials research activities of all members of the Materials Research Center at

Northwestern. Presented herein are brief descriptions of the various individual research programs active during the 1969/70 year, arranged alphabetically by the name of the principal investigator. Also included are lists of publications and invited talks stemming from the research and the names of research associates and graduate students affiliated with each project.

DOCTOR OF PHILOSOPHY DEGREES AWARDED IN THE FIELD OF MATERIALS

JUNE COMMENCEMENT 1970

Teruaki Aoki. Materials Science. "Anomalous Transport Properties of β' -Phase 3rd-Transitional-Metal Alloys". AF, ARPA.

Mahendra S. Bapna. Materials Science. "Plastic Deformation of Quench-Hardened Gold". AEC, ARPA.

Melvin Budzol. Chemistry. "The Radiation Chemistry of Polyethylene and Polypropylene Oxide". AEC, ARPA.

Dipankar Chandra. Materials Science. "Spinodal Decomposition in Fe-Cr Using Mössbauer Spectroscopy". AISI, Inland Steel, ARPA.

Bernard A. Coyle. Chemistry. "The Structures of Three Inorganic Complexes". TA, NDEA, NSF.

Joseph K-S. Fang. Chemistry. "Mechanism of Proton Transfer in Water". TA, NIH, ARPA.

John E. Gragg, Jr. Materials Science. "The Internal Structure of Guinier-Preston Zones in Aluminum-5 Atomic Percent Silver". NSF, ARPA.

Edward L. Hall. Materials Science. "A Neutron Diffraction Study of the Magnetic Properties of MnAs and MnAs_{0.92}P_{0.08}". NSF, AISI, WPM.

Paul D. Hambourger. Physics. "Size-Dependent Oscillatory Magnetoresistance in Cadmium". NUF, ARPA.

Daniel A. Hill. Physics. "Dynamic Polarization of Protons in Polymers at Low Temperatures". TA, ARPA.

Robert E. Hollins. Chemistry. "Molecular Beam Mass Spectra and Pyrolyses of Pentaborane(9), Tetraborane Carbonyl, and Pentaborane(11); Formation and Mass Spectrum of B₄H₈". TA, ARPA.

Rex S. Itoga. Electrical Engineering. "Electrical and Optical Properties of TlS_{0.5}Se_{0.5} and TlSe". TA, ARPA.

George F. Jackson, III. Chemistry. "The Stereomutation of Phosphorus and Arsenic". NSF, NIH, TA.

Michael G. Kovac. Electrical Engineering. "Enhanced X-ray Photoelectric Emission from Metal-Insulator Layers". NIH, AEC.

Lawrence L. Mack. Chemistry. "Molecular Beams of Macroions". TA, NIH, ARPA.

Donald A. Miller. Electrical Engineering. "Dielectric and Dilatation Studies on Single Crystal Phenanthrene in the Temperature Range of 24 to 82°C". TA, ARPA.

- K. Nagasubramanian. Chemical Engineering. "Effect of Residence Time Distribution in Branched Polymer Formation". Phillips Petroleum, Monsanto Company, NSF, ACS, ARPA.
- John A. Obersteuffer. Physics. "The Chemical and Magnetic Structure of Single Crystal Alpha Manganese". ARPA.
- V. R. Parameswaran. Materials Science. "Dislocation Mobility in Lead and Lead-Indium Alloy Single Crystals". ARPA.
- John W. Rau, III. Electrical Engineering. "Some Optical and Galvanomagnetic Properties of GeAs and GeAs₂". ARPA.
- Leroy W. Schroeder. Chemistry. "Nature of the Strong Hydrogen Bond in ClHCl- and BrHBr-". TA, ARPA.
- James E. Sickles. Materials Science. "Threshold and Production of Length Change Introduced into Pure and Doped MgO Irradiation Below 90°K". NDEA, AEC.
- Judith K. Stalick. Chemistry. "Some Structures of Five-Coordinate Transition Metal Complexes". NSF, TA.
- Jacob J. Stiglich, Jr. Materials Science. "Interdiffusion and Defect Structure in NiO + CoO Solid Solutions". AF.
- Basil I. Swanson. Chemistry. "Structures, Molecular Vibrations, and Bonding in Boron Trihalide Adducts of Acetonitrile". TA, NSF, NDEA.
- Dogan Turhan. Civil Engineering. "A Dynamic Theory of Directionally Reinforced Composites". ARPA, IIE.
- Akio Urakami. Materials Science. "Effect of Li Additions on Mechanical Properties of Mg Base Single Crystals in Basal and Prismatic Slip". WPM, ARPA.
- William C. Uy. Chemical Engineering. "Viscosity and Normal Stresses in Linear Polyvinyl Acetate Systems". WPM, ARPA, NSF, ACS.
- Leonard E. Voelker. Civil Engineering. "Transient Stress Response of a Laminated Composite to a Transverse Loading". NASA, AF.
- Ernst D. Von Meerwall. Physics. "Nuclear Magnetic Resonance and Magnetic Susceptibility Study of the Vanadium-Manganese Alloy System". ARPA.
- Donald E. Weber. Physics. "Electron Microscopic Study of Heavy Ion Irradiation Damage of Thin Gold Film". TA, AEC.

Research supported by agencies as indicated:

ACS, American Chemical Society
 AEC, Atomic Energy Commission
 AF, Air Force Office of Scientific Research

AISI, American Iron and Steel Institute
ARPA, Advanced Research Projects Agency
IIE, International Institute for Education
NASA, National Aeronautics and Space Administration
NDEA, National Defense Education Act
NIH, National Institutes of Health
NSF, National Science Foundation
NUF, Northwestern University Fellowship
Inland Steel, Inland Steel Company Fellowship
Monsanto, Monsanto Company Fellowship
Phillips Petroleum, Phillips Petroleum Company Fellowship
TA, Northwestern University Teaching Assistantship
WPM, Walter P. Murphy Fellowship, Northwestern University

APPLICATION OF CONTINUUM THEORIES TO DESCRIBE INHOMOGENEOUS AND ANELASTIC BEHAVIOR OF MATERIALS

J. D. Achenbach
Professor, Department of Civil Engineering

J. C. S. Yang
Postdoctoral Research Associate

V. Varatharajulu
Ph.D. Thesis Research

Objective

To evolve suitable continuum theories to describe phenomenologically the dynamic gross properties of inhomogeneous materials. Particular attention is devoted to the influence of thermal and viscoelastic effects, nonlinear material behavior and large deformations. Inhomogeneous materials such as directionally reinforced composites are used more frequently in a variety of systems, particularly in aerospace and deep-submergence technology. This study will supply information on the behavior of directionally reinforced composites under dynamic loading conditions.

Approach

The fundamental balance laws of mechanics and the theory of thermodynamics of simple materials, in conjunction with a smoothing principle, are used to develop a continuum theory which describes on a phenomenological level the dynamic behavior of directionally reinforced composites.

Progress

Studies were completed on the thermodynamics of a continuum with microstructure and on the interaction of electromagnetic fields with deformable bodies. A theory was developed to describe the dynamic behavior of a viscoelastic laminated composite, including the effects of temperature variations. A nonlinear theory was derived to describe the mechanical behavior of a laminated composite consisting of alternating layers of two homogeneous materials subjected to large deformations.

PUBLICATIONS

"Relativistic Continuum Theory for the Interaction of Electromagnetic Fields with Deformable Bodies," R. A. Grot, J. Mathematical Physics, 11, 109 (1970).

"Large Deformations of a Laminated Composite," R. A. Grot and J. D. Achenbach, Int. J. Solids and Structures, 6, 641 (1970).

INVITED TALKS

"The Dynamic Behavior of Directionally Reinforced Composites," Science Center/Aerospace and Science Group, North American Rockwell Corporation, Thousand Oaks, California, November 1969.

"Waves and Vibrations in Reinforced Composites," Michigan Technological University, Houghton, Michigan, December 1969.

DYNAMICS OF VISCOELASTIC AND REINFORCED SOLIDS

J. D. Achenbach
Professor, Department of Civil Engineering

Y. S. Lai
Ph.D. Thesis Research

This research is supported by the Office of Naval Research.

Objective

Current research is concerned with waves and vibrations in plates and cylinders fabricated of laminated media. The objective is to establish those conditions for which dynamic effects arising from the internal structuring of the solid, i.e., the lamination, predominate effects due to the overall geometrical configuration of the body.

Approach

A continuum model is employed to describe the mechanical behavior of the laminated composite. In deriving the governing equations for the continuum model, approximate displacement expressions for the discrete elements are used to compute potential and kinetic energies for a volume element of the laminated composite. By means of a smoothing operation, energy densities for the composite are derived. Applications of Hamilton's principle, where certain subsidiary conditions enter through the use of Lagrangian multipliers, yields displacement equations of motion, constitutive equations and boundary conditions.

Progress

Various versions of a new theory for laminated media, the effective stiffness theory, were investigated. For certain simple cases results were compared with exact solutions. It was found that the effective stiffness theory describes in a satisfactory manner the dynamic behavior of laminated media.

PUBLICATIONS

"Field Equations Governing the Mechanical Behavior of Layered Circular Cylinders," F. H. Chou and J. D. Achenbach, AIAA Journal, 8, 1444 (1970).

"Crack Propagation Generated by a Horizontally Polarized Shear Wave,"
J. D. Achenbach, J. Mech. Phys. Solids, 18, 245 (1970).

"Wave Propagation in Laminated and Fiber-Reinforced Composites," in
Mechanics of Composite Materials, Pergamon Press, p. 237 (1970).

"Propagation of Second-Order Thermomechanical Disturbances in Visco-
elastic Solids," Proc. IUTAM Symposium East Kilbride (ed. B. A.
Boley), Springer-Verlag, p. 1 (1970).

INVITED TALK

"Fracture Generated by Transient Waves," University of Notre Dame,
Notre Dame, Indiana, May 1970.

TRANSIENT WAVE PROPAGATION IN FIBER REINFORCED COMPOSITES

J. D. Achenbach
Professor, Department of Civil Engineering

S. J. Fang
Ph.D. Thesis Research

This research is sponsored by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

Objective

The propagation of transient stress waves in composites is investigated both analytically and experimentally. Particular attention is devoted to local dynamic effects and short-time phenomena. The causes of delamination at the interfaces are investigated for dynamic loading conditions.

Approach

For loads of short duration and for short times the reflection and transmission are traced through the discrete elements of the composite. For longer times a continuum model is employed to describe the dynamic response of the composite body.

Progress

It was shown that due to the inhomogeneous composition and for the ratios of material properties of the constituents that are used in actual composites large tensile stresses and thus delamination through tensile failure may occur.

PUBLICATIONS

- "Stress Waves in a Laminated Medium Generated by Transverse Forces,"
L. E. Voelker and J. D. Achenbach, J. Acoust. Soc. Am., 46,
1213 (1969).
- "Separation at the Interface of a Circular Inclusion and the Surrounding
Medium Under an Incident Compressive Wave," J. D. Achenbach,
J. H. Hemann and F. Ziegler, J. Appl. Mech., 37, 298 (1970).
- "Asymptotic Analysis of the Modes of Wave Propagation in a Solid Cylinder,"
J. D. Achenbach and S. J. Fang, J. Acoust. Soc. Am., 47, 1282
(1970).

INVITED TALK

**"Methods Based on Dynamic Similarity for Problems of Elastic Wave
Propagation," Illinois Institute of Technology, Chicago, Illinois,
February 1970.**

CLEAVAGE REACTIONS OF GROUP IV-M METAL-METAL BONDS

A. L. Allred

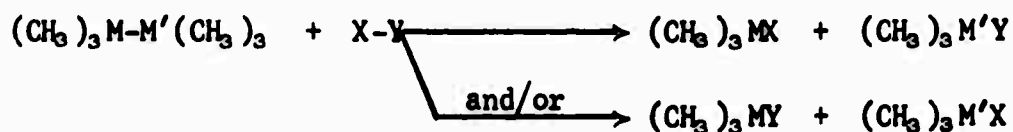
Professor, Department of Chemistry

C. Frank Shaw, III

Ph.D. Thesis Research (Completed)

Objective

To investigate the cleavage of unsymmetrical metal-metal bonds with unsymmetrical reagents including iodine monochloride, hydrogen chloride and trifluoroiodomethane. Of interest were factors which determine the mode of cleavage:



Approach

The reactions of $(\text{CH}_3)_3\text{M}-\text{M}'(\text{CH}_3)_3$, where M and M' are C, Si, Ge and Sn, were carried out in sealed tubes and/or a high vacuum system. Products were identified by gas chromatography, nuclear magnetic resonance and infrared spectroscopy.

Progress

The iodine monochloride cleavage reactions of M-M' bonds lead in each case to the products predicted by the generalization of Hard and Soft Acids and Bases and not in general to the products having the larger bond polarities. For example:



The other conceivable products $((\text{CH}_3)_3\text{SnCl} + (\text{CH}_3)_3\text{GeI})$ of this reaction would be predicted from a consideration of bond polarities. While thermodynamic data are scarce, the experimental results indicate that the products are thermodynamically controlled and not kinetically controlled. The silicon-germanium bond is surprisingly stable toward hydrogen chloride. For HCl and $(\text{CH}_3)_3\text{GeSn}(\text{CH}_3)_3$, carbon-tin and germanium-tin cleavages occur to about the same extent.

DIASTEREOTOPIC NONEQUIVALENCE IN ASYMMETRIC TIN COMPOUNDS

A. L. Allred
Professor, Department of Chemistry

D. V. Stynes
Ph.D. Thesis Research

Objective

The goals of this are (a) to determine those factors which influence rates of inversion at tin, and (b) to synthesize and resolve asymmetric tin compounds. Despite a tremendous amount of work involving optically active carbon-containing compounds, no asymmetric compound of tin has been resolved.

Approach

Classical organometallic procedures were employed for the syntheses of benzylmethylneophylphenyltin, methylphenylbenzyltin iodide, benzylmethylneophyltin iodide, benzylmethylneophyltin chloride and methylneophylphenyltin iodide. Diastereotopic nonequivalence was investigated by nuclear magnetic resonance.

Progress

A comparison of the NMR spectra of the above asymmetric tin compounds indicates that the large anisotropy of the phenyl ring is important in establishing a sufficient difference in shielding for diastereotopic nonequivalence to be observed. All three diastereotopic groups in benzylmethylneophyltin chloride are observably anisochronous in nonpolar solvents. Analysis of the coalescence of all three sets of diastereotopic peaks provides definitive evidence for a rapid inversion of configuration of the asymmetric tin center in trialkyltin halides. The concentration dependence of the mean lifetime of the asymmetric tin center indicates a second-order process. A five-coordinate halogen-bridged intermediate apparently is involved in the observed halogen exchange accompanying inversion.

INVITED TALK

"Electron Spin Resonance Studies of Organometallic Compounds,"
Ohio State University, February 1970.

HIGH OXIDATION STATES OF ZINC, CADMIUM, AND MERCURY

A. L. Allred
Professor of Chemistry

M. O. Kestner
Ph.D. Thesis Research

Objective

The goal of this research is to stabilize and investigate the properties of the Zn^{+3} , Cd^{+3} , and Hg^{+3} ions both as dopants in oxide lattices and as the central element in complexes.

Approach

Attempts are being made to obtain high oxidation states by "valence inductivity". It is well-known that if certain metal oxides are either deposited on the surface of a different oxide or dissolved in the second oxide, the crystal structure of the film or the solid solution tends to be determined by the structure of the host oxide, and the added metal ions on the surface or in the crystal tend to have the same oxidation states as the metal ion of the host oxide. A second approach to high oxidation states involves the use of ligands which tend to stabilize the tripositive ions of silver and nickel.

Since Zn^{+3} , Cd^{+3} and Hg^{+3} are d^0 ions, isoelectronic with Cu^{+2} , electron spin resonance is the choice tool for the detection of these ions.

Progress

The coprecipitation of Al_2O_3 and CdO , followed by heating from 500° to 1000° in an oxygen atmosphere, gave a material which exhibited a weak electron spin resonance spectrum reminiscent of the e.s.r. spectrum of Cu^{+2} . Attempts are being made to maximize the concentration of Cd^{+3} in Al_2O_3 . A comparable e.s.r. signal was observed for the product of the persulfate oxidation of ethylenbisbiguanidezinc sulfate. The tripositive ion, ethylenbisbiguanidesilver(III) is well-known and preparable by a comparable oxidation of silver(I) complex. Currently, attempts are being made to oxidize macrocyclic-tetranitrogen complexes of nickel, zinc and cadmium both with persulfate and by electrochemical techniques.

PUBLICATION OF RESEARCH DESCRIBED IN PREVIOUS MRC ANNUAL TECHNICAL REPORTS

"Isotope Exchange in the GeH_4 -KOD- D_2O System," A. L. Allred and R. L. Deming, Inorg. Nucl. Chem. Letters, 6, 39 (1970).

SYNTHESIS OF GLOBULAR MOLECULES

A. L. Allred
Professor, Department of Chemistry

S. A. Kandil
Research Associate (Completed)

C. F. Shaw, III
Ph.D. Thesis Research (Completed)

This research was partially supported by the National Institutes of Health.

Objective

To synthesize the large, spherical, highly hindered molecule, tetra-t-butyltin and to observe physical and chemical properties of this compound. The general goal is the synthesis and characterization of new materials.

Approach

The planned synthesis of tetra-t-butyltin involves the reaction of tin tetrachloride and t-butyllithium. The cryoscopic constant will be measured by the standard sealed tube technique and also calculated from ΔH fusion. Heat capacity measurements will be used to infer the temperatures at which (1) molecular rotation begins, (2) phase changes, if any, occur, and (3) methyl and t-butyl rotations are important, if they are important. The second moment and the spin relaxation time, T_1 , will be measured as a function of temperature. The crystal system will be determined by x-ray diffraction.

Progress

Several t-butyltin derivatives including the tri-t-butyltin chloride and iodide were synthesized. Experiments designed for the synthesis of tetra-t-butyltin by the reaction of tri-t-butyltin halide with t-butyllithium led to the isolation of hexa-t-butylditin. On the other hand, other organolithium and Grignard reagents yielded the expected products. A critical study was undertaken to establish the structural requirements in the organotin derivatives for the normal substitution to occur preferentially over the coupling reaction. Two series of monomers of the type $R_2R'SnX$ were synthesized for this purpose: Series I, where $R = tBu$; $R' = C_6H_5$, $p-CH_3C_6H_5$, $C_6H_5CH_2$, $n-Bu$; and Series II, where $R' = t-Bu$; $R = C_6H_5$, $C_6H_5CH_2$, $n-Bu$; $X = Cl, Br, I$. Coupling was observed with Series I, and Series II yielded

the normal products. A description of these results is in press (J. Chem. Soc. A.).

PUBLICATIONS

"Nonbonded Interactions in Organometallic Compounds of Group IVB,"
C. F. Shaw, III and A. L. Allred, Organometallic Chem. Reviews,
5, 95 (1970).

"Apparatus for Crystallization at Low Temperatures in an Inert
Atmosphere," C. F. Shaw, III and A. L. Allred, J. Chem. Ed.,
47, 164 (1970).

SOME EXACTLY SOLVABLE PROBLEMS IN MAGNETISM

M. Bailyn

Professor, Department of Physics

J. Chen

Ph.D. Thesis Research

This research is jointly supported by the National Science Foundation and the Advanced Research Projects Agency.

Objective

The objective of this project is to see if something can be said rigorously in the theory of spin magnetism, and in so doing, gain some insight into the general features of the phenomena and into the usual approximations made.

Approach

We start from the limiting case of a one-dimensional loop of atoms with one electron per atom all with the same spin, the ferromagnetic limit. With this as a reference state, we consider certain classes of excitations, the simplest being a one spin-flip excitation, the next simplest two spin-flips, and so on. The general procedure is extremely simple: expand the wave function of the excited state in a complete set of Wannier spin-flip states, substitute into the Schrödinger equations, and set up equations for the coefficients in the expansion. The resulting equations are then Fourier analyzed. Alternatively, the resulting equations are solved by a method generalized from the Bethe method used in the problem of an anti-ferromagnetic chain.

Progress

Last year, the one-spin flip problem was completely solved for two cases: (1) the linear loop with one-band with nearest neighbor Wannier interactions, and (2) the two-band loop with nearest neighbor interactions in a band and on-site interactions between the bands. These two cases have been published this past year. Since then, we have worked the problem of a one-band loop with long range interactions, and some nearest neighbor two and three dimensional problems. The long range calculation has been completed and accepted for publication, the many dimensional problem is still being calculated. We have also looked at the case of the two-electron, one hole excitation, and the two spin-flip excitations, but these are orders of magnitude more difficult to solve than the one-spin flip case. To investigate these more complicated excitations we looked into the feasibility of solving the problem by the Bethe method. This method enables the wave functions to be put in a simple form, and has been used in other related problems. We have been able to re-solve the

one-spin flip problem by this method and as complicated as the spectrum is, the Bethe solution in its completely different form gives precisely the same result, as must of course be. The other excitations have been studied now by the Bethe method, but as yet the formulation gives results still too complicated to be satisfactory.

PUBLICATION

"Ferromagnetic Spin Excitations in a One-Band Metallic Loop," J. Chen and M. Bailyn, Phys. Rev., B, 3030 (1970).

PUBLICATIONS ON COMPLETED RESEARCH PREVIOUSLY REPORTED IN MRC ANNUAL TECHNICAL REPORT

"Kondo Effect in the Ruderman-Kittel-Kasuya-Yosida Interaction," R. Bresemann and M. Bailyn, Phys. Rev., B, 334 (1970).

STRUCTURE SENSITIVE PROPERTIES OF SOLIDS - GALVANOMAGNETIC EFFECTS IN β' -PHASE INTERMETALLIC COMPOUNDS

J. O. Brittain

Professor, Department of Materials Science

T. Yoshitomi

Ph.D. Thesis Research

Objective

The objective of this research is to study the electronic transport properties of equiatomic 3d-transition-metal aluminides, (β' -phase), which have CsCl type crystal structure, and to ascertain the nature of the magnetic elements in the compounds.

Approach

Noting the anomalous galvanomagnetic effects of NiAl such as resistance minimum phenomena, negative magnetoresistance and field dependent Hall coefficient, which can be explained qualitatively in terms of so-called s-d interaction, we measure electrical resistivity, magnetoresistance and Hall coefficient on $\text{Co}_x\text{Ni}_{1.5-x}\text{Al}_{1.5}$ and $\text{Fe}_x\text{Ni}_{1.5-x}\text{Al}_{1.5}$ as a function of temperature and composition ($0 \leq x \leq 0.5$).

In the case of these alloys, the mechanism of the anomalous transport phenomena would be more directly attributed to the localized magnetic moment at the transition metal atoms in the alloys rather than to the deviation of composition from the stoichiometry which was employed to explain the existence of s-d interaction in β' -NiAl systems.

Progress

Electrical resistivity measurements have been made on the alloys described above. All samples containing Co showed the resistance minimum phenomena at low temperatures. The depth of the minimum increases as the Co concentration increases. No resistance maximum phenomena were observed in this system. The resistance minimum phenomena was also observed in the alloys with Fe additions of less than 0.4. The depth of minimum was largest at $x = 0.05$ and resistance maximum following the minimum was observed in some alloys of this system. For both systems the temperature dependence of the resistivity exhibited Kondo-type logarithmic dependence, but deviated from it at very low temperatures.

PUBLICATION

"Electronic Structure of β' -NiAl," Y. Yamaguchi, T. Aoki, and J. O. Brittain, J. Phys. Chem. of Solids, 31, 1325 (1970).

STRUCTURE SENSITIVE PROPERTIES OF SOLIDS - MECHANICAL BEHAVIOR OF COMPOSITE MATERIALS

J. O. Brittain

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P. Columbovski

Ph.D. Thesis Research

Objective

Composite materials are a developing class of materials with improved properties at high temperatures. An investigation of the temperature and structural dependence of the mechanical behavior of composites is the main objective of this research.

Approach

Controlled directional solidification will be utilized to prepare composites in eutectic alloys. This technique will produce a distribution of rods or lamellae in a continuous matrix. The nature of the distribution can be varied through control of the growth rate and the temperature gradient at the solid-liquid interface during solidification. The structures will be characterized by quantitative metallography techniques in conjunction with optical and electron microscopy. The mechanical behavior of suitable prepared and characterized specimens will be determined by tensile testing at various temperatures and strain rates. Some effort will be devoted to elucidate fracture processes.

Progress

A directional controlled solidification apparatus has been designed and is under construction. Means for controlling the solidification rate and the temperature gradient of the eutectic alloys have been incorporated in the apparatus. Apparatus for the elevated temperature tensile tests have also been assembled.

STRUCTURE SENSITIVE PROPERTIES OF SOLIDS - OPTICAL PROPERTIES IN β' -PHASE INTERMETALLIC COMPOUNDS

J. O. Brittain

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K. Tamura

Ph.D. Thesis Research

Objective

This investigation is directed toward discerning the influence of the defect state in intermetallic compounds upon various properties.

Approach

The optical properties have been evaluated from intensity data on a specially designed reflectometer and polarizers in the wavelength range of approximately 0.25 to 2.5μ . Moreover an InSb detector for wavelength range of 1 to 5μ and vacuum UV spectrophotometer for wavelength range of 0.1 to 0.3μ are being used to work for normal reflectance measurements to extend the range of measurements. Since the optical properties represent superposition of free electron behavior, interband transitions and plasma effects, a separation of the individual contributions is a desired objective.

Progress

The optical properties of β' -NiAl, and -CoAl, NiGa and CoGa have been investigated, and it has been reported that only NiAl had a compositionally dependent interband transition at photon energy of 2.5eV. The optical properties of ternary alloys $\text{Ni}_x\text{Co}_y\text{Al}_{1-x-y}$, $\text{Ni}_{1-x-y}\text{Al}_x\text{Ga}_y$, $\text{Ni}_x\text{Fe}_y\text{Al}_{1-x-y}$ and $\text{Ni}_x\text{Cu}_y\text{Al}_{1-x-y}$ of mainly stoichiometric composition ($x + y = 0.5$) have now been measured in the wavelength range of 0.1 to 2.5μ . The three peaks in ϵ_2 observed with $\text{Ni}_{1-x-y}\text{Al}_x\text{Ga}_y$ alloys are linearly compositionally dependent. However, measurements with $\text{Ni}_x\text{Co}_y\text{Al}_{1-x-y}$ and $\text{Ni}_x\text{Fe}_y\text{Al}_{1-x-y}$ alloys revealed that all three peaks in ϵ_2 (2.4, 4.1 and 5.3 eV) are compositionally independent when they are not masked by free electron behavior. In $\text{Ni}_x\text{Cu}_y\text{Al}_{1-x-y}$ alloys, the 2.4eV peak moved to a lower photon energy with increasing copper content.

PUBLICATION

"The Optical Properties of β' -Phase CoAl, and NiGa," D. Kiewit and J. O. Brittain, J. Appl. Phys., 41, 710 (1970).

STRUCTURE SENSITIVE PROPERTIES OF SOLIDS - PRISMATIC DISLOCATION LOOP FORMATION AND GROWTH IN β' -NiAl

J. O. Brittain

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G. W. Marshall

Ph.D. Thesis Research

This research is partially supported by Northwestern University.

Objective

This work aims at gaining an understanding of the nature and origins of the dislocation structure observed in β' -NiAl as a function of composition and thermal history.

Approach

Thin foils from oriented single crystals and polycrystals of representative compositions of β' -NiAl are examined using transmission electron microscopy to determine the variations in structure resulting from different thermal treatments. Experiments designed to control thermal conditions and composition are used to characterize the dislocation source and mechanism of dislocation loop growth.

Progress

Prismatic dislocation loops and spirals on (100) planes with Burgers vectors of a (100) type have been observed in near stoichiometric and Al-rich alloys of β' -NiAl. The critical thermal history for the development of the prismatic dislocation loop structure in single crystals has been determined. The structure can be explained in terms of the operation of Bardeen-Herring dislocation sources. The phenomenon has not been observed in Ni-rich alloys or in alloys of small grain size. Attempts to control dislocation sources by varying the heat treating atmosphere in Al-rich single crystals has failed. Impurities in the starting material for crystal growth apparently are responsible for the presence of the dislocation sources, although selective additions of suspected impurities to melts of high purity Ni and Al have not produced the Bardeen-Herring dislocation sources.

Research is being carried out to determine the following:

- 1) the spatial distribution of loops produced as a function of heat treatment and composition; 2) if the loops are of vacancy or interstitial type; and 3) the factors determining the shape of the loops and the mechanism of loop growth.

STRUCTURE SENSITIVE PROPERTIES OF SOLIDS - STRUCTURE AND PROPERTIES OF POLYMERS

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W. W. Graessley
Professor, Departments of Chemical Engineering and Materials Science

F. S. Myers
Ph.D. Thesis Research

This research is partially supported by Northwestern University.

Objective

The objective of this work has been to survey various thermal and mechanical properties of blends of Lexan Polycarbonate and Polysulfone P-1700 as functions of composition and thermal history and to relate these results to observed compositional variations in microstructure.

Approach

Lexan and P-1700 have been solution blended to a number of intermediate compositions, and the blended material reclaimed from solution by solvent evaporation from thin, cast films. These films then were ground to a fine molding powder and molded into bulk form by compression and injection molding processes.

Thermal expansion and softening temperatures were obtained from linear dilatometry; tensile tests were performed at 0°, 25°, and 65°C at a single strain rate; and a low frequency investigation of the secondary β peak region of the mechanical relaxation spectrum was conducted by a free decay technique.

Microscopic evaluation of microstructure was performed principally by optical microscopy on deformed and undeformed etched material and on tensile fracture surfaces.

Progress

A marked variation in microstructural texture was found among material from the three molding techniques. This variation was found to exhibit considerable influence on the tensile behavior, but the effects were less evident in the other tests performed.

From the microscopy it was determined that the blends formed a two phase system at all compositions investigated. A phase inversion was found near 75 wt/o P-1700, and it was also in this region that notable property changes were observed in softening temperatures, tensile moduli, and the mechanical relaxation. The thermal and tensile property changes reflect the transition from Lexan to P-1700 being the continuous, load bearing component.

The effect of composition on the relaxation process is not as macroscopically obvious. The broad, single β peak found in Lexan and P-1700 was found to divide into two peaks in 75 wt/o unannealed material. With annealing, the higher temperature peak was absorbed into the high temperature side of the primary peak, yielding in a fully annealed sample, the single peak found in P-1700. It is speculated that the occurrence of the second relaxation peak was due to the strain associated with the intermixing of molecular chains associated with the inversion composition.

While apparently incompatible in the thermodynamic sense, the microscopic investigation of deformed and fractured surfaces indicates considerable interfacial interaction in all compositions.

MICROWAVE INVESTIGATIONS OF SEMICONDUCTORS

M. E. Brodwin

Professor, Department of Electrical Engineering

H. Brodsky

Ph.D. Thesis Research

K. Chou

Ph.D. Thesis Research (IIE Fellow)

S. Kahn

Ph.D. Thesis Research (Northwestern University Support)

W. Tempelmeyer

Ph.D. Thesis Research (Northwestern University Support)

Objective

The purpose of this project is to observe and analyze phenomena appearing at microwave frequencies in certain solids. Problem areas are chosen which combine both scientific and applied objectives. Representative of these areas are: instability in drifted plasmas, microwave hypersound in paraelectric solids and microwave-acoustic-transducers.

Approach

The theoretical and experimental studies are designed to answer specific questions about each of the phenomena studied. For example, our studies in drifted plasma are directed toward developing definite experiments to resolve theoretical questions. The oscillation in InSb under pulsed electric field conditions is currently explained by stating that the emission originates in the high density and high density gradient regions produced by Suhl effect concentration. An experiment has been devised to test these speculations and preliminary results indicate that these speculations are incorrect, and a different theoretical explanation is required for the observed instabilities. In the same area, a well known dispersion relation has been used to predict instability in drifted plasmas. This relation has never been experimentally verified and our study of it suggests that its range of validity may be quite small. Thus, an experiment is being planned to examine this dispersion relation.

We are also examining a new phenomenon: the interaction of microwave phonons with paraelectric solids. Here we are searching for the first experimental evidence of a postulated microwave resonant absorption in crystalline KCl with small additions of substitutional hydroxyl ion. This absorption arises from transitions between dipole energy levels and is analogous to an acoustic absorption in a paramagnetic system.

Recent interest in applications of microwave phonons to radar and communications has prompted a review of the transducer mechanism at these frequencies. We have instituted a study of a new, more efficient transducer structure.

Progress

The work on hot electrons in InSb and other semiconductors is at the point where large area diffused contacts are being deposited on samples. The instrumentation for this problem has been completed.

The interaction of microwave phonons with paraelectric solids has reached the point where a rather complex experimental apparatus has been constructed, samples prepared, and final refinements being carried out.

The microwave-acoustic transducer study is at the point where the feasibility analyses is being completed.

ANISOTROPIC ELECTRICAL CONDUCTIVITY IN POLYMERIC SOLIDS

S. H. Carr

Assistant Professor, Departments of Materials Science and
Chemical Engineering

S. Deo

M.S. Thesis Research

Objective

A number of polymers have been synthesized during the past decade with the purpose of creating materials with low electrical resistivity. In most cases the electrical conductivity was measured on bulk samples but the solid state molecular organization was not investigated. Because the electrical conductivity in these polymers will probably be anisotropic, control over morphology is the likely way to maximize their usefulness. Thus, it is the aim of this research to establish principles in the relationship between electrical conductivity and morphology.

Approach

Two lines of pursuit are being followed, the first of which involves the manufacture of microelectrodes suitable for measuring electrical conduction in polymer single crystals. Photolithographic Techniques for making miniature integrated circuits are being employed to make an array of many closely spaced gold conductors on sapphire chips. Single crystals can then be deposited on the chip by drying them from suspension in xylene. Current-voltage relationships at a variety of temperatures will be measured to obtain information on the conduction mechanisms.

The other approach to this project involves the synthesis of polymer from tetraiodophthalic anhydride and the substitution of pyridine for chlorine in poly(epichlorohydrin). Each repeat unit in this latter polymer has the capacity to complex with TCNQ molecules blended into the sample. A study of morphology by electron microscopy and diffraction techniques will reveal what levels of molecular organization exist in both polymers.

Progress

Chips for use as microelectrodes are being prepared. Apparatus for synthesizing the polymers is being assembled and the electrical conductivity cell is under construction.

MOLECULAR STRUCTURE IN POLYOLEFIN FIBERS

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P. Fung

M.S. Thesis Research

Objective

Fibers made from crystallizable polymers undoubtedly derive much of their mechanical properties from the character of their molecular order. The crystal texture of these fibers is controlled considerably by conditions imposed on the melt spinning, take-up, and post-drawing processes. Furthermore, the molecular weight distribution in the polymer effects the morphology.

The objective of the present research is the characterization of the morphology of melt spun fibers from polyolefin samples in which the molecular weight distribution has been modified and the identification of all major parameters relating to the strength of these synthetic fibers.

Approach

Control of the molecular weight is being achieved primarily by a technique developed in preceeding work on polyethylene crystallization from solution (see publication). This technique uses a bed of crushed NaCl to selectively extract the fraction of the sample presumed to contain the largest molecules, and another sample is enriched with the extracted material. Fibers are then formed by extruding the polyethylene through a small diameter capillary in the Instron Melt Rheometer. Fibers may then be subjected to a variety of post-drawing conditions. Characterization follows with tensile measurements and electron microscopy.

Progress

Equipment necessary to melt-spin and take-up fiber has been assembled and used. Apparatus for extracting high molecular weight material has been constructed and polyethylene samples have been made. Techniques for surface replication of the fibers, suitable for electron microscopy, have been developed. Preliminary results suggest a pronounced sensitivity of the fiber production processes to molecular weight distribution, but differences in the resulting morphology and fiber strength seem subtle.

PUBLICATIONS

"Relationship Between Self-Seeded and Epitaxial Crystallization from Polymer Solutions. A Possibly New Technique for Molecular Weight Separation," S. H. Carr, A. Keller, and Eric Baer, J. Polymer Sci., Part A-2, 8(9), 1467 (1970).

DIFFRACTION STUDIES OF MATERIALS

J. B. Cohen

Professor, Department of Materials Science

M. Kirk

Ph.D. Thesis Research

J. Gragg

Ph.D. Thesis Research (Completed)

Objective

X-ray studies of defects in solids.

Approach

Measurements of diffuse x-ray scattering and the intensities of Bragg peaks.

Progress

Measurements of the diffuse intensity from Al-5 at.pct Ag (aged at 110°C) in a volume of reciprocal space has permitted the separation of this intensity into that due to local order and that due to atomic displacements. The scattering near superstructure positions, previously thought to be due to order within G.P. zones, has been shown to be due to distortions associated with the zones. Computer simulation with the Warren local order parameters indicates that the zones are octahedra (containing 68 at.pct Ag), not spheres, as was generally thought to be the case.

The differences in strength and resistivity of zones formed above 170°C, where these are more nearly spherical, and below 170°C appear to be due to the decrease in Ag concentration (and hence, the distortion due to the zones) at the higher temperatures.

With Professor Davidson's group, the radial density distribution of partially crystalline isotactic polystyrene was obtained; this was compared to our previous results on isotactic and atactic amorphous phases, and the crystalline structure. It appears that as the regularity increases (atactic amorphous-isotactic amorphous-isotactic partially crystalline-crystalline) helical portions of the long chain decrease their pitch and their separation.

Work continues on studies of electron damage of Ni₃Mn, to detect whether replacement collisions really occur. Single crystals have been grown and cut, and are being heat-treated. Because little is known of the diffusion rates or ordering kinetics in this alloy some preliminary

data on ordering were obtained to guide heat-treatments. An attachment has been built for x-ray studies of the intensity of superstructure reflections. In addition to allowing alignment of the crystal at low temperatures, it can be attached to a Van de Graff generator for in situ bombardment.

PUBLICATIONS

"Optimum Procedures for Determining Ultra-Fine Grain Sizes," J. B. Cohen, W. Paulson, and J. E. Hilliard, 15th Sagamore Army Materials Research Conference, Syracuse University Press, Syracuse, New York (1970) pp. 73-98.

"An X-ray Study of a Possible Phase Transition in Phenanthrene," J. B. Cohen, K. Chiang, P. Forsyth, L. Morrison, and J. Kauffman, Phys. Rev. Letters, 30A, 531 (1969).

"The Nature of Long-Range Order in $\text{Cu}_{2+x}\text{Au}_{1-x}$," J. B. Cohen and P. Gehlen, J. Appl. Phys., 40, 5193 (1969).

"The Order-Disorder Transformation" in "Phase Transformations," ASM, Metals Park, Ohio, 1970, pp. 561-620.

INVITED TALKS

"The Physical Meaning of Local Order," Gordon Conference on Physical Metallurgy, Tilton, New Hampshire, August 24, 1970.

EFFECTS OF THERMO-MECHANICAL TREATMENTS ON THE SUBSTRUCTURE IN METALS AND ALLOYS

J. B. Cohen

Professor, Department of Materials Science

R. Marion

Ph.D. Thesis Research

M. A. Zemitis

M.S. Thesis Research (NSF Trainee)

This research is supported by the Office of Naval Research.

Objective

Studies of the effects of thermal and mechanical treatments on faulting, macro-stresses, microstrains and subgrain sizes in metals and alloys.

Approach

Analysis of x-ray diffraction peak shape and position.

Progress

Work continues on the anomalous effect in residual stress measurements with x-rays. (It is known that in compression, tension, or bending, a macro-stress is measured when other methods indicate that there is none; also, the sign of the stress and/or its magnitude can vary from peak to peak used in the measurement.) We have found a similar effect after moderate rolling. It has been proposed that this effect is related to texture in the specimen (F. Bollenrath, V. Hauk, and W. Weidemann, Archiv fur das Eisenhutt., 38, 793 (1967)); this has been confirmed qualitatively, and a simple way to include the effects of texture quantitatively has been developed. This method does not involve the measurement of a pole figure and is simple enough to be of general use. Quantitative tests are underway, for Cu₃Au and a 1045 steel. At the same time, we are exploring further the conditions for which this effect can be serious.

When as cast Al-Si alloys are deformed at room temperature, the peaks of the Si phase sharpen, and continue to do so with time after deformation. This effect appears to be due to thermally activated relaxation of dislocation arrays in the Al matrix around Si particles. In Ag-Si, the Si peaks broaden extensively; due to the lower fault energy of Ag, compared to Al, such rearrangement is not as easy.

Quantitative studies with the Ag-Si system are being made with two different morphologies for the Si phase, spheres and needles. Fourier analysis of line-broadening is being carried out under load in tension and after release of the load.

A small tensile rig, to be used in both studies, has been constructed for the diffractometer.

PUBLICATION

"Broadening and Shifting of Diffraction Profiles from Antiphase Boundaries or Faults in a B2 Structure," J. B. Cohen and R. Rothman. Proceedings of the 3rd Bolton Landing Conference on Ordered Alloys, Claitor's Publishing Division, Baton Rouge, Louisiana, 1970, pp. 149-167.

LOCAL ATOMIC ARRANGEMENTS IN ALLOYS AND INTERMETALLICS

J. B. Cohen

Professor, Department of Materials Science

P. Bardhan

Ph.D. Thesis Research

H. Berg

Ph.D. Thesis Research (Cabell Fellow)

K. Paavola

M.S. Thesis Research

This research is supported by the National Science Foundation.

Objective

Theoretical and experimental studies of local atomic arrangements, their topology and their effect on properties.

Approach

Inter-relationships between local order parameters and their control of local atomic arrangements are studied theoretically. Experimental measurements of diffuse scattering, their interpretation in terms of the local structure, and the role of this structure in determining properties.

Progress

We have been able to show (without any assumptions) that the first two or three pair probabilities or local order parameters (α 's) very tightly confine the values for nearest-neighbor triplets or quadruplets in an f.c.c. structure. For example, for Cu_3Au at 450°C the all-copper quadruplet fraction could range from 0.0 to 0.75, but the known α 's confine the range to 0.11-0.16. The equivalence due to symmetry of many triplets or quadruplets in any group of atoms plays a key role in this confinement, but in the f.c.c. structure there are many more symmetry conditions than needed for this. We are now exploring whether the confinement exists also in b.c.c. alloys for which the symmetry is lower.

A program for computer simulation of a 2-d alloy has been written to examine the local arrangements of Onsager's exact solution of the Ising model, and the effects of various approximations on these arrangements.

Computer simulation of the local atomic arrangements in an Fe-6 at pct Mo alloy (with pair probabilities from our x-ray study of this system) has proved particularly interesting. The Mössbauer spectra from this system after aging at 550°C had been studied previously (H. L. Marcus, M. E. Fine, and L. H. Schwartz, J. Appl. Phys., 38, 4750 (1967)). Extra peaks appear due to Fe atoms with different numbers of Mo atom neighbors. An interpretation in terms of 0, 1 or 2 Mo neighbors in the first two neighbor shells is given in Table 1 (a); this is the model the authors employed. It is not in agreement with the computer simulations. Furthermore, the peak for Fe atoms with no Mo neighbors should be larger in the actual alloy than for a random alloy, as there are Mo clusters, but the reverse is true (compare columns 2 and 4). A more successful explanation was obtained by including Mo atom neighbors in three shells, Table 1 (b). These simulations should thus be particularly useful in interpreting the complex Mössbauer spectra from alloys. The data and simulations also provide some information on the lack of hardening due to the zones and the alloy "softening" in this system.

Table 1. Comparison of Atomic Distributions with Interpretation of Mössbauer Spectra in Ref. 2, for Fe-6.1 at. pct Mo.

(a)

Fraction of Fe atoms with indicated number of Mo neighbors in <u>1st</u> and <u>2nd</u> shell.	Random (Calculated)	Clustered, from Atomic Distributions	From Ref. 1
0	0.438	0.498	0.384
1	0.402	0.296	0.561
2	0.160	0.133	0.055
> 2	--	0.072	--

(b)

Fraction of Fe atoms with indicated number of Mo atoms in <u>1st</u> three shells.	Random (Calculated)	Clustered, from Atomic Distributions	From Ref. 1
0	.25	0.36	0.384
1 or 2 (with 1 in each of two shells).	.64	0.55	0.561
2 in either <u>1st</u> , <u>2nd</u> , or <u>3rd</u> shell.	.11	0.09	0.055

Our field-ion microscopy of partially ordered CoPt₃ has been completed. (This work was done by Mr. Berg at Pennsylvania State University with Profs. Mueller and Tsong.) Rods of Pt several atoms in length on wrong sites in $\langle 100 \rangle$ and $\langle 110 \rangle$ directions have been found. Also there are at least two dimensional Pt-rich regions and small out-of-phase regions. We are trying to determine if these larger regions are three dimensional. Single crystals have been obtained and are being heat-treated. (When this is done, the diffuse x-ray scattering will be measured and computer simulations from the measured pair-probabilities will be compared to the FIM studies.)

A set of programs have been developed and tested to enable a PDP 8/L computer to run diffuse scattering experiments. After an initial dialogue with the operator concerning physical limits on the angles of tilt of a crystal and other variables of the experiment, the computer moves three motors to establish a position in reciprocal space, records counts at this position corrected for dead time, and moves on. Points outside the physical limits are skipped and a constant check is made of the direct beam's intensity and any specimen movement. The data, on paper tape, is then fed to another code which places it in a format suitable for an other program for the CDC 6400; this separates intensity into its components due to local order and size effects, and then performs Fourier inversions for local-order parameters, etc.

PUBLICATIONS

"The Order-Disorder Transformation," in "Phase Transformations," ASM, Metals Park, Ohio, 1970, pp. 561-620.

"A Brief Review of the Properties of Ordered Alloys," J. B. Cohen, J. Mat. Science, 4, 1012 (1969).

INVITED TALK

"The 'Gestalt' of Local Order," Battelle Conference on Critical Phenomena, Gstaad, Switzerland, September 9, 1970.

PHASE TRANSFORMATIONS IN MACROMOLECULAR MATERIALS

T. Davidson

Assistant Professor, Departments of Materials Science and Chemical Engineering

T. Natarajan

Ph.D. Thesis Research

A. Scigliano

M.S. Thesis Research (O.A.S. Fellow)

Objective

The mechanism and kinetics of phase changes in polymeric solids including melting, crystallization and solid-solid transformations are under investigation.

Approach

Several solid polymers exhibit solid-solid structural transformations. A prominent example is the pair of transitions at 19° and 30°C in polytetrafluoroethylene. These transformations result in a change in crystal structure from triclinic to hexagonal and an unwinding of the macromolecular helix. The kinetics of these transformations can be measured thermogravimetrically by following the change of specific volume with time.

Melting and crystallization of polymers is affected by a number of parameters, notably the molecular weight distribution and the presence in the distribution of both very long and very short molecules. Poly(ethylene oxide) has been chosen as a model system in which to investigate the effects of molecular weight on melting and solidification. Binary mixtures which differ widely in mean molecular weight are being used to test the hypothesis of fractionation during crystallization.

Progress

A model for the 19 degree transition in PTFE has been developed and is being used to predict the kinetics of the transition. Experiments using a recording thermobalance are underway to provide data for a test of the model.

Measurements of the transition temperatures and heats of fusion in the poly(ethylene oxide) system are being performed using differential scanning calorimetry.

STRUCTURE OF HIGH POLYMERS IN THE SOLID STATE

T. Davidson

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W. S. Park

M.S. Thesis Research (Stauffer Fellow)

Objective

This research is directed toward understanding the structure of high polymers in the crystalline and semi-crystalline states.

Approach

The study of effects due to crystallinity in polymers is usually complicated by the coexistence of crystalline and non-crystalline regions in macromolecular solids. We have studied polymers crystallized under high pressure which leads to extended-chain structures with a minimum of non-crystalline material. Another class of polymers which exhibits high crystallinity consists of macromolecules which have polymerized and crystallized simultaneously. Particle-form polyethylene constitutes such a material.

When this polymer is synthesized over catalysts of supported transition metal oxides at low temperatures, the macromolecules crystallize during the act of polymerization. Effectively, this is a transformation from gaseous ethylene monomer to crystalline solid polymer. Since polyethylene crystals are formed directly by this gas-solid reaction, the usual entropic and kinetic barriers to crystallization are absent and enhanced crystal growth is the result.

Progress

Through the use of scanning electron microscopy, a series of unique structural features has been discovered in particle-form polyethylene. Four distinct structural elements have been found in the 0.05 to 10 micrometer range. Helical crystals are present in lengths up to 7 micrometers. Further details of the microstructure are being actively investigated.

INVITED TALKS

"Extended-Chain Polymer Crystals," Department of Chemical Engineering Colloquium, Northwestern University, February 2, 1970.

"The Microstructure of Crystalline Polymers by Electron Microscopy," State Microscopical Society of Illinois, Chicago, February 27, 1970.

THE STRUCTURE OF AMORPHOUS POLYMERS

T. Davidson

Assistant Professor, Departments of Materials Science and Chemical Engineering

S. M. Wecker

Ph.D. Thesis Research

Objective

The principal objective of this research is to characterize the structural features of high polymers in the glassy state. Particular attention is given to the effect of solidification conditions and macromolecular tacticity on the resulting polymer glasses.

Approach

Samples of polystyrene are compression molded from well-characterized material. By varying the cooling rate, passage through the glass transition can be controlled. Structural information on the glasses is obtained by wide-angle X-ray scattering using monochromatic radiation and digital counting techniques. The corrected X-ray intensity data is Fourier transformed to yield a radial distribution function (RDF) which indicates the spacings between groups on a given macromolecule and the distances separating neighboring molecules in the glassy state.

Progress

Four distinct X-ray maxima are observed and these have been assigned to nearest and next-nearest neighbors in the chain, and to combinations of inter- and intra-chain spacings. Regardless of cooling rate, all atactic polystyrene samples used in the experiments have identical densities, scattering patterns, and radial distribution functions. The quenched isotactic polymer produced samples of greater density but with the same RDF as that of the atactic material. For comparison to the quenched glasses, a sample of isotactic polystyrene was annealed to develop 20 percent crystallinity. The RDF for this semi-crystalline material shows a sharpening of the diffraction peaks and shifts of the third and fourth RDF peaks in opposite directions relative to the quenched polymer. These opposing trends of inter- and intra-chain packing are being examined by computer modeling to determine whether variations in macromolecular helicity can account for the observed structural changes.

SUPRAMOLECULAR STRUCTURE AND MICROPLASTICITY IN POLYTETRAFLUOROETHYLENE

T. Davidson

Assistant Professor, Departments of Materials Science and Chemical Engineering

T. Natarajan

Ph.D. Thesis Research

D. K. Weber

M.S. Thesis Research (Completed)

This research is principally supported by the National Science Foundation.

Objective

This research seeks to determine the microstructure of polytetrafluoroethylene (PTFE) both "as-polymerized" and as modified by heat treatment. The relation between structure and the micromechanics of deformation in polymers is being pursued using PTFE as a model system.

Approach

Electron microscopy provides information on the microstructure of both "as-polymerized" and sintered PTFE through the use of replica techniques. Specimens are subjected to deformation by rolling and to tensile testing over a range of conditions from 77°K to ambient temperature. It was originally hypothesized that deformation in a partially crystalline polymer such as PTFE would occur by yielding in the non-crystalline regions combined with plastic deformation of the crystals.

Progress

Our studies on the tensile deformation of PTFE have shown that at cryogenic temperatures both above and below the "glass II" transition at 160°K, yielding occurs principally in the non-crystalline regions. Only when severely deformed by rolling does plastic deformation of the crystalline phase become an active mode of deformation. These findings indicate the importance of a two-phase structure for promoting high strength in polymeric materials at low temperatures.

By means of electron microscopy, a microstructure of fibrils and large lamellar crystals have been shown to co-exist in as-polymerized PTFE. This supports the concept for simultaneous polymerization and crystallization in the synthesis of polytetrafluoroethylene.

CIRCULAR DISLOCATION LOOPS AND MOVING DISLOCATIONS IN MULTI-PHASE MATERIALS

J. Dondurs

Professor, Department of Civil Engineering

M-S. Lee

Ph.D. Thesis Research

N. J. Salamon

Ph.D. Thesis Research (NDEA Trainee)

Objective

The objective is to investigate the behavior of dislocations near the boundary between two phases with different elastic constants.

Approach

The approach is by idealizing the discrete lattices as elastic continua.

Progress

Among the various problems under study, significant progress can be reported on two. First, the elastic fields were obtained for screw and edge dislocations that move with a constant velocity parallel to the boundary between the two phases. Presently, the very tedious calculations required to find the energy are being carried out. Second, a key discovery was made which allows one to analyze effectively dislocation loops and other configurations in the vicinity of the interface between the two phases. Thus, it was found that the fields induced by loops in the inhomogeneous material can be obtained by the straightforward process of applying certain differential operators to the fields caused by the dislocation loops in a homogeneous material. This result is now being exploited for circular loops.

DISLOCATIONS IN LAYERED MATERIALS, SURFACE LAYERS AND THIN FILMS

J. Dundurs

Professor, Department of Civil Engineering

M-S. Lee

M.S. Thesis Research (Completed)

K. C. Tsai

Ph.D. Thesis Research

Objective

The aim is to derive the displacement field, energy and force for dislocations in layered materials, surface layers and thin films.

Approach

The required elasticity solutions are obtained by use of Fourier transforms.

Progress

This study is motivated by the need to know more about the properties of dislocations in multi-layered materials, such as composites and directionally solidified alloys, and similarly in surface layers and thin films because of their use in electron microscopy. The geometry of these problems dictates the use of Fourier transforms for finding the various field quantities. This approach yields results expressed in terms of integrals which can only be evaluated numerically. The solutions for several problems had been obtained before, and the past year was spent chiefly to arrive at the numerical evaluation of the quantities that are of particular interest in applications. Because of the importance of such results in electron transmission microscopy, particular attention was given to the displacement field induced by screw and edge dislocations in a thin layer.

ELASTIC FIELDS IN COMPOSITE MATERIALS

J. Dundurs

Professor, Department of Civil Engineering

C. F. Hsieh

Ph.D. Thesis Research (Completed)

Objective

The goal of this research is to study how stresses and related quantities, such as the interaction energy and force, acting on a dislocation in a composite material, depend on the elastic constants of the various phases.

Approach

Assuming elastic behavior, use is made of the field equations and boundary conditions in elasticity.

Progress

The conditions under which stresses, energy of a dislocation and the force on a dislocation show a reduced dependence on the elastic constants of the phases were established and suitable composite parameters introduced earlier. Recently, new composite parameters were invented. These parameters are preferable because they admit a direct interpretation in terms of the uniaxial and voluminal compliances of the two phases. Furthermore, they are convenient for making various results on composite materials tractable physically, and they have already been adopted by several other authors in their studies.

PUBLICATIONS

"Dependence on Elastic Constants of Some Residual and Dislocation Stresses in a Composite," J. Dundurs and C. F. Hsieh, Developments in Theoretical and Applied Mechanics, Vol. 4, edited by D. Frederick, Pergamon Press, Oxford, pp. 103-115 (1970).

"Some Properties of Elastic Stresses in a Composite," J. Dundurs, Recent Advances in Engineering Science, Vol. 5, edited by A. C. Eringen, Gordon and Breach, New York, pp. 203-216 (1970).

PEIERLS STRESS AND STABILITY OF DISLOCATION ARRAYS

J. Dundurs

Professor, Department of Civil Engineering

N. T. Adelman

Ph.D. Thesis Research (NSF Trainee)

M-S. Lee

Ph.D. Thesis Research

Objective

The goals of these studies are to improve the expression for the Peierls stress and to study the stability characteristics of various dislocation arrays, particularly pile-ups.

Approach

Dislocation theory based on a linearly elastic medium is used.

Progress

A modified expression for the Peierls stress was obtained by following a suggestion made by Nabarro and employing a method used by Huntington in his work on the core of an edge dislocation. The resulting expression for the Peierls stress yields a much less drastic dependence of the stress on Poisson's ratio than the previous results.

When dislocations are driven against an obstacle by applied stresses, and they pile up, each individual dislocation experiences repulsion from its neighbors and, consequently, has the tendency to leave or pop out of the array. Screw dislocations are held in the array only by the Peierls forces, and the question of whether they will or will not leave the array is essentially a stability proposition. A pile-up of screw dislocations was found to be unstable if the distance d between the two leading dislocations becomes too small, or

$$d < k (\mu b / \tan \theta)^{\frac{1}{2}}$$

where k is approximately $1/2$, μ is the shear modulus, b is the Burgers vector and $\tan \theta$ is the initial slope of the Peierls force. Using this result, one can subsequently investigate the stability of various pile-up arrays for which the spacing among the dislocations is known from other work. Thus, for instance, it is possible to derive a simple condition on the applied stress under which a single-ended pile-up becomes unstable. Several other types of pile-up arrays also have been investigated. Presently, the study has turned to the various possibilities for blunting of pile-ups and the relation of pile-up stability to fracture.

PUBLICATIONS

"Stress Concentrations Due to Edge Dislocation Pile-ups in Two-phase Materials," J. Dondurs and M-S. Lee, Scripta Metall., 4, 313 (1970).

ELASTIC FIELDS IN CONTACTING BODIES

J. Dondurs

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N. A. J. Jabri

M.S. Thesis Research

K. C. Tsai

M.S. Thesis Research

This research is primarily supported by the National Science Foundation.

Objective

The objective is to investigate general properties of elastic fields in contacting bodies and to derive certain specific solutions for purposes of illustration.

Approach

The treatment is essentially theoretical, but some experiments involving photoelasticity and interferometry are anticipated.

Progress

This work is only of peripheral interest in materials science, but it is reported here because the rather unlikely chain of discoveries leading to new results in contact problems started with the study of dislocations interacting with inhomogeneities. The sequence of observations from dislocation to contact problems is too long and too technically involved for reporting in brief and, therefore, only the results obtained will be mentioned. When two bodies are placed in contact, the geometries of the bodies establish some initial contact. In case the initial contact is over a surface, the contact may either expand (advance) or shrink (recede) upon loading. Many examples can be given for contacts that recede. It was discovered that the elastic fields for receding and advancing contacts have entirely different properties regarding their dependence on the level of loading and relation to the elastic constants. Thus, when the contact recedes, the extent of contact is independent of the level of loading, and the elastic fields are much less sensitive to changes in elastic constants than when the contact advances.

INTERACTION BETWEEN DISLOCATIONS AND INCLUSIONS

J. Dundurs

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N. T. Adelman

M.S. Thesis Research (Completed) (NSF Trainee)

M. Comninou

M.S. Thesis Research

A. C. Gangadharan

M.S. Thesis Research (Completed)

This research is primarily supported by the National Science Foundation.

Objective

The general aim of this work is to investigate quantitatively the elastic interaction between dislocations and various second-phase inclusions.

Approach

Theoretical treatment of the elastic interaction between dislocations and inclusions requires first the solution of the appropriate elasticity problem. Once the elastic fields are known, the interaction can be studied using either the interaction energy or the force on the dislocation.

Progress

The elasticity solution for an edge dislocation near a circular inclusion with a slipping interface was obtained by A. C. Gangadharan in 1966. At that time, however, the results could not be made physically meaningful because of the mathematical complexities involved. Using some later discoveries pertaining to the general dependence of the interaction energy on the elastic constants, these difficulties have been overcome, and a complete physical interpretation of the results has been achieved.

To analyze the interaction when a dislocation is in a general position with respect to an inclusion, one must know how the given inclusion disturbs the rather complicated stress field that the dislocation induces in the homogeneous material. In contrast, this information is needed only for a uniform stress field when the dislocation is far away from the inclusion, allowing one to study problems for which the general case is out of reach. The study of the far interaction with elliptical inclusions has been completed, and the attention has recently been shifted to spherical inhomogeneities.

PUBLICATIONS

"Edge Dislocation Near an Inclusion with a Slipping Interface," J. Dundurs and A. C. Gangadharan, J. Mech. Phys. Solids, 17, 459 (1969).

INVITED TALKS

"Elastic Interaction Between Dislocations and Inhomogeneities," University of Waterloo, Ontario, Canada, July 1970.

MAGNETIC INTERACTIONS IN SIMPLE MODEL SYSTEMS

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H. P. Davis

Ph.D. Thesis Research

Objective

Simple models for magnetic interactions have played a very useful role in parametrizing experimental data; however, relating the model parameters to the more fundamental charge and spin densities of even very simple systems has proved to be difficult. These difficulties continue to grow, rather than diminish, as the magnetic resonance, neutron scattering, optical measurements, etc., improve in quality and quantity, since simple specialized models cannot describe both the structure and breadth of the available data. Our objective here is to study very simple model systems by all means available in order to intercompare the predictions of more or less rigorous calculations with those of simplified models, and thus to extend their usefulness.

Approach

The ring of N equally spaced hydrogen atoms has been used in a number of previous studies as a vehicle for studying magnetic interactions in periodic systems. One has available the molecular orbital or energy band approaches to the electronic structure, the Heisenberg and spin wave models for spin structure, the Anderson model hamiltonian approach, etc. Our method is to determine the full multiplet structure of the ring (for $N < 20$) in a limited energy interval by a variational calculation, and to study how the Heisenberg and spin wave models can best be adapted to fit the true collective excitations of the system.

Progress

The non-orthogonal gaussian orbital program of Professor A. Frost was adapted for computing states of the H_N ring of hydrogen atoms. Both single determinant and configuration interaction calculations (fully optimized) were performed to obtain the spectrum and wave functions for states ranging between the ferromagnetic and antiferromagnetic limits. As a result of the simple form of the model wave function analytic expressions for magnetic splittings are obtained; the results have been interpreted in terms of the influence of second, third, and more distant neighbor interactions. The limits of accuracy

of the Heisenberg model in describing the magnetic spectra were analyzed by a least squares fitting procedure; the effect of truncating the model to nearest neighbors only is investigated. Analytic expressions are given for eigenvalues of the complete Heisenberg Hamiltonian, including all coupling parameters, for the ring of six atoms. The variation of effective exchange parameters with bond length is displayed in a paper submitted for publication.

ELECTRONIC STRUCTURE OF IONIC AND COVALENT MATERIALS

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G. S. Painter

Oak Ridge National Laboratory

This research is primarily supported by the Air Force Office of Scientific Research and the Atomic Energy Commission.

Objective

There has been considerable interest in the magnetic and optical properties of transition metal and rare earth compounds. These properties have been largely characterized in the past from an atomic or molecular (ligand field) point of view; our objective is to develop methods adequate to a reasonable description of the crystal. Methods for generating crystal potentials and obtaining the energy band structure of metals are fairly well developed; however, this is far from the case in ionic and covalent materials. The strongly aspherical crystal coulomb potential makes the usual "muffin-tin" approximation practically useless, and the problem of finding a suitable "effective exchange" potential is unsolved—certainly the free electron approximation used successfully in metals must be modified. Beyond this is the most important question of whether one electron orbitals for these materials are best represented as Bloch waves, localized states, or a mixture of both.

Approach

Work on the localized or molecular cluster approach to these problems is described elsewhere in this Report; here we concentrate on the energy band aspect. Since we must treat rather complicated aspherical potentials, we are developing a variational-numerical method of a very general form which is being optimized in the course of application to specific materials. The approach can be extended to self-consistent calculations with a given local or two-body potential; the chief problem being the determination of compact and accurate representations of the charge density. The solution of this problem also greatly simplifies the calculation of optical absorption and x-ray scattering amplitudes.

Progress

The band structure and wave functions for lithium metal, diamond, and graphite have been obtained (nonself-consistently) and the results

compared with experiment and previous calculations; further work on these materials is aimed toward better understanding of optical properties and x-ray scattering data. Preliminary fits to the charge density have been obtained to carry forward these calculations, and to permit steps toward self-consistency. Results obtained for SiC and TiC are being analyzed to determine the relative importance of d-bands in the carbides, and to study their sensitivity to changes in the exchange potential. The variational-numerical method is used in this work has proved to be accurate and reliable; some experiments are in progress to determine the optimum procedure for augmenting the tight-binding basis, in studying the higher "excited bands." Band structures of the optically interesting LiF and MgO have been explored, and a detailed interpretation of their absorption spectra will be forthcoming.

PUBLICATIONS

"A Direct Numerical Method for the Energy Band Problem: Preliminary Results for Li," G. S. Painter and D. E. Ellis, Int. J. Quantum Chem., 3S, 801 (1970).

"Electronic Band Structure and Optical Properties of Graphite from a Variational Approach," G. S. Painter and D. E. Ellis, Phys. Rev., B1, 4747 (1970).

INVITED TALK

"Discrete Variational Method For the Energy Band Problem," IBM Conference on Band Theory, Yorktown Heights, N. Y., August 1970.

IMPEDANCE CHARACTERIZATION OF TRANSDUCERS

M. Epstein

Associate Professor, Department of Electrical Engineering

A. Nalamwar

M.S. Thesis Research

Objective

Development of improved techniques in the characterization of electro-acoustic transducers.

Approach

An analytical technique is used to determine the impedance of an elastic surface-wave transducer from insertion loss measurements. It is based on Guillemin's Real Part Sufficiency and the properties of Hilbert transforms.

Progress

Comparison of analytical results using digital computation with experimental results shows that the susceptance or reactance of a transducer can be evaluated with far greater accuracy than is possible with most refined experimental techniques. Since the static capacitance of a transducer can be measured quite accurately at low frequencies, it appears that the present method can become significant in defining accurately the equivalent circuit of the transducer.

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THIN-FILM SURFACE-WAVE TRANSDUCERS

M. Epstein

Associate Professor, Department of Electrical Engineering

F-C. Liao

Ph.D. Thesis Research (Institute Research Fellow)

Objective

The objective of this research is to study the possible application of the strain-sensitivity of thin-film field-effect transistors for surface-wave transducers with particular emphasis on nonlinear characteristics and their utilization in signal detection.

Approach

Thin-film field-effect transistors, using cadmium sulphide and cadmium selenide, were fabricated on glass substrates. The acoustic surface waves were generated by using the techniques of mechanically variable delay lines (as described in the report on Wideband Transduction Techniques for Acoustic Surface-Wave Devices).

Progress

Although thin-film transistors with high transconductance were obtained ($g_m \approx 10,000$ micromhos), it appears that the functions of surface-wave transduction and field-effect amplification are incompatible; i.e., the characteristics of the material (high piezoelectric coupling and field effect) cannot be attained simultaneously. Hence, this work has been discontinued and, instead, another research program was initiated to develop a surface-wave phonon amplifier using vacuum-deposited and re-crystallized films of indium antimonide.

ELECTRON-BEAM SENSING OF ACOUSTIC SURFACE WAVES

M. Epstein

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S. G. Joshi

IIT Research Institute

R. J. Serafin

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A. P. van den Heuvel

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N. Zueffle

Ph.D. Thesis Research (Institute Research Fellow)

This research is supported by the Office of Naval Research.

Objective

The objective of this research is the study of secondary electron emission from surfaces of strained piezo-electric crystals for applications in the detection of elastic surface waves.

Approach

To utilize the modulation of secondary electron current by the strain-produced potential on the surface of a piezo-electric crystal.

Progress

Apparatus commonly used in electronic image storage was designed and constructed. Experiments with a surface-wave device designed for a 6 MHz pulsed carrier frequency show that the secondary electron current is modulated by the signal envelope of the elastic surface wave. The apparent rectification of the rf pulse has not as yet been satisfactorily explained.

PUBLICATIONS

"Electron Beam Sensing of Surface Elastic Waves," M. Epstein, S. G. Joshi, R. J. Serafin and A. P. van den Heuvel, Proc. IEEE, 58, 253 (1970).

WIDEBAND TRANSDUCTION TECHNIQUES FOR ACOUSTIC SURFACE-WAVE DEVICES

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M. E. Motamedi

Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

Study electro-acoustic transduction on piezoelectric crystals leading to elastic surface-wave devices which are capable of processing wideband (large information) signals.

Approach

Elastic surface-wave transducers were fabricated utilizing photolithographic techniques. Structures consisting of log-periodic arrays of interdigitated electrodes were fabricated directly on substrates of LiNbO_3 and glass; those with glass substrates were employed in the investigation of mechanically variable delay lines.

Progress

Fourier analysis of an approximate electric field distribution at the interdigital transducer was found to provide a useful method in the synthesis of filter functions of elastic surface-wave devices. The analytical model showed remarkably good agreement with experimental results. The performance of the log-periodic interdigital transducer as to its frequency response and impedance was shown to be considerably better when compared with conventional resonant (uniform) interdigital transducers. Wideband and resonant interdigital transducers fabricated on glass substrates were used to propagate elastic surface waves on LiNbO_3 crystals. It was shown that such a technique can lead to the design of mechanically variable delay lines with additional insertion loss not exceeding 14db per transducer.

A technique to measure insertion loss (radiation resistance) of transducers was devised which eliminates the effects of the measuring apparatus.

SHUBNIKOV-DE HAAS EFFECT IN N-DOPED GRAY TIN

A. W. Ewald

Professor, Department of Physics

M. J. Horowitz

Ph.D. Thesis Research

Objective

To use the unusually large amplitude magnetoresistance oscillations in gray tin to study the energy dependence of the effective mass, the electron screening of ionized impurities and the spin splitting of Landau levels.

Approach

The temperature, magnetic field and orientation dependences of the amplitude are measured in samples ranging in donor concentration from 10^{18} to 10^{19} donor atoms per cm^3 . Analysis yields the Dingle temperature (which measures the effect of ionized impurity scattering on the amplitude), and the energy dependence of the light electron effective mass. Spin splitting of magnetoresistance peaks in samples having a sufficiently low Dingle temperature is used to evaluate the effective g factor and its anisotropy.

Progress

Improvements have been made in the signal detection equipment and in sample selection and handling techniques. The circuit noise level has been greatly reduced, optimum etching conditions have been determined, and re-etching of samples down to ~ 0.1 mm diameter has been accomplished through probe re-design and improvement in sample mounting techniques. Magnetoresistance oscillations have been observed in samples heavily doped with arsenic. The oscillations exhibit spin splitting and other behavior similar to that of the previously investigated Sb-doped samples.

PUBLICATIONS

"Spin Splitting of Landau Levels and the Effective g Factor in Gray Tin,"
B. L. Booth and A. W. Ewald, Phys. Rev., 186, 770 (1969).

INTERBAND MAGNETOREFLECTION OF GRAY TIN

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Lincoln Laboratory, MIT

C. R. Pidgeon
National Magnet Laboratory

R. J. Wagner
Naval Research Laboratory

This experiment was done at the Francis Bitter National Magnet Laboratory with support from the Department of the Air Force, the U. S. Air Force Office of Scientific Research, the National Science Foundation and the Advanced Research Projects Agency.

Objective

To observe the optically induced transitions between Landau levels in an elemental solid having the inverted (gray tin) band structure and to make a detailed comparison of the data with theory and evaluate important band structure parameters.

Approach

Magnetoreflexion traces were made by sweeping the magnetic field (to a maximum of 100 kOe) at fixed photon energies. The latter ranged from 0.05 to 0.55 eV and sample temperatures ranged from 1.5 to 85°K.

Progress

Two sets of interband transitions were observed. One set consists of transitions from the Γ_8^+ valence-band Landau levels to the Γ_8^+ conduction-band levels. The second set consists of transitions from a lower valence band, Γ_7^- , to the Γ_8^+ conduction band. The $\Gamma_8^+ - \Gamma_7^-$ separation was found to be 0.413 eV, and independent of temperature over the measurement range. The directly determined band-edge masses are 0.028 m_e for the Γ_8^+ conduction band, 0.195 m_e for the Γ_8^+ valence band, and 0.058 m_e for the Γ_7^- valence band. The $\vec{k} \cdot \vec{p}$ interaction parameter E_p and the valence-band spin-orbit splitting were found to be 24.0 eV and 0.80 eV, respectively.

PUBLICATIONS

"Interband Magnetoreflexion of α -Sn," S. H. Groves, C. R. Pidgeon, A. W. Ewald and R. J. Wagner, Proceedings of the Ninth International Conference on the Physics of Semiconductors, Nauka Publishing House, Leningrad, p. 43 (1968).

"Interband Magnetoreflexion of α -Sn," S. H. Groves, C. R. Pidgeon, A. W. Ewald and R. J. Wagner, J. Phys. Chem. Solids, 31, 2031 (1970).

PIEZORESISTANCE AND PIEZO-HALL EFFECTS IN GRAY TIN

A. W. Ewald

Professor, Department of Physics

H. Busta

Ph.D. Thesis Research (ARPA Support)

P. Ho

M.S. Thesis Research

This research is primarily supported by the National Science Foundation.

Objective

To separate the degenerate conduction and valence bands in gray tin through the application of uniaxial compressive stress and thereby produce and study typical semiconductor behavior at unusually low temperatures. Application of tensile stress should cause overlap of the same bands, and a second objective is the investigation of the resulting semimetal or semiconductor behavior.

Approach

Oriented single crystals are subjected to uniaxial compression or tension. Conductivity and Hall coefficient are measured in the temperature range from 1.3 to 100°K.

Progress

A paper based on B. J. Roman's compressive stress measurements and analysis has been prepared. The principal results are the following. Measurements were made on high purity ($N_D \sim 5 \times 10^{14} \text{ cm}^{-3}$) and lightly-doped ($2 \times 10^{15} \leq N_D \leq 2 \times 10^{17} \text{ cm}^{-3}$) n-type gray tin subjected to oriented stresses (in [001]^D and [111] directions) up to $3 \times 10^9 \text{ dynes/cm}^2$. Density-of-states expressions were developed to account for the severe band anisotropies imposed by the strain, and these were employed to determine the band splitting at $k = 0$ from the Hall coefficient of the high purity samples above 15°K. Shear deformation potentials of $b = -2.3 \pm 0.5 \text{ eV}$ and $d \approx -4.1 \text{ eV}$ were obtained by this procedure. The Hall coefficient of three high purity samples below 10°K was analyzed to find the stress-dependent ionization energy and an independent determination of $b = -2.0 \text{ eV}$ was obtained. The stress dependence of the impurity band mobility was found to be consistent with Sladek's model for exchange jumping between adjacent impurity sites. The piezoresistance of lightly doped samples was attributed to the increased effectiveness of ionized impurity scattering caused by a stress-enhancement of the conduction band density-of-states mass.

Mr. Busta has undertaken the extension of the measurements to higher magnetic fields, higher purity samples and to tensile (as well as compressive) stress. During the past year he has learned the techniques, developed by Mr. Roman, for sample preparation and for the measurements. Mr. Ho has been engaged in material purification and characterization.

MECHANICAL BEHAVIOR OF Mg BASE-Li ALLOY SINGLE CRYSTALS

M. E. Fine

Professor, Department of Materials Science

A. Urakami

Ph.D. Thesis Research (Completed)

Objective

On adding Li to Mg which is hexagonal, alloy hardening occurs for basal slip, alloy softening occurs for prismatic slip. The objective was to obtain experimental information which would lead to an understanding of this difference in behavior between the two slip systems.

Approach

The yield and flow characteristics in tension of basal and prismatic slip in Mg and Mg-Li alloys to 15.7 at.% Li were measured from 4.2 to 450°K versus the strain rate. Solute-dislocation interactions were investigated by strain aging. The dislocation structures after deformation were observed by transmission electron microscopy. Yield drop effects were observed and studied.

Progress

This research has been completed. The experimental details were reported last year. The interpretation will now be reported. The alloy hardening and the strain aging yield drop which occur for basal slip in Mg base-Li alloys were attributed to a size effect interaction between Li atoms and dislocation. The prismatic slip alloy softening in this system was attributed to an interplay of the effect of Li on the dislocation width and in catalyzing double kink formation, the mechanism by which the dislocations surmount the Peierls barrier. In Mg the dislocations are thought to initially lie on the basal plane and the dislocation cores are thought to be split. In order for screw dislocations to slip onto the prism plane a constriction needs to form. Addition of Li is thought to reduce the core splitting, thus it becomes easier for the dislocations to slip onto the prism plane. Once dislocations have been formed on the prism plane then their flow stress is thought to be determined by the stress necessary to overcome the Peierls barrier. This occurs by nucleation of double kinks. A calculation was made showing that a size effect interaction between screw dislocations and misfitting solute atoms catalyzes double kink formation thereby reducing the flow stress. Confirming evidence for the effect of Li on the dislocation width comes from the effect of Li on the screw dislocation configuration. They are straight in Mg and low Mg alloys. They are helical in the high Mg alloys.

PUBLICATIONS

"Electron Microscopic Investigation of Prismatic Slip in Mg-10.5 at.% Li Single Crystals," A. Urakami and M. E. Fine, Acta Met., 18, 87 (1970).

"Influence of Misfit Centers on Formation of Helical Dislocations," A. Urakami and M. E. Fine, Scripta Met., 4, 667 (1970).

"Effect of Li on Mechanical Properties of Mg Base Single Crystals in Basal and Prismatic Slip," 2nd International Conference on The Strength of Metals and Alloys, Conference Preprints, p. 87, ASM sponsored, with A. Urakami and M. Meshii, August-September 1970.

INVITED TALK

"Effect of Li on Mechanical Properties of Mg Base Single Crystals in Basal and Prismatic Slip," 2nd International Conference on The Strength of Metals and Alloys, Asilomar Conference Grounds, Pacific Grove, California, August-September 1970.

MECHANICAL BEHAVIOR OF Ti-BASE Al ALLOYS

M. E. Fine

Professor, Department of Materials Science

T. Sakai

Ph.D. Thesis Research

Objective

The objective is to determine the effect of Al on the mechanical flow properties of Ti in prismatic and basal slip and to develop an understanding of the mechanisms of plastic deformation and mechanical strengthening which are operative.

Approach

The mechanical flow characteristics in compression and tension in Ti-Al alloys up to 10 at.% Al will be measured as functions of temperature, strain rate, and crystallographic orientation. Transmission electron microscopy will be used to study the dislocations.

Progress

Results in polycrystalline samples of Battelle Ti, Ti-3.9 at.% Al and Ti-7.4 at.% Al show that the yield stress increases with concentration of Al in agreement with previously published results. The yield stress in compression was 10 to 30% higher than the yield stress in tension except in the alloys at 77°K. The strain rate sensitivity ($d\tau/d \ln \dot{\gamma}$, where τ is the flow stress and $\dot{\gamma}$ is the strain rate) in tension is much higher than that in compression and there is a considerable difference in the temperature dependence. In the Ti-7.4 at.% Al the tension $d\tau/d \ln \dot{\gamma}$ increases on cooling to 77°K while it decreases on compression.

ALLOYING EFFECTS IN STEELS

M. E. Fine

Professor, Department of Materials Science

S. C. Kolesar

Ph.D. Thesis Research (Inland Steel and ARPA Supported)

D. Leemans

Ph.D. Thesis Research (Inland Steel Supported)

This research is jointly supported by Inland Steel Corporation and the Advanced Research Projects Agency.

Objective

Alloy softening in Fe has been widely observed at low temperatures. A general study of this important phenomenon from an experimental and theoretical point of view has been undertaken.

In ferritic Fe-base Ni-Al alloys, dilute in Ni and Al, an (Fe,Ni)Al precipitate phase having the CsCl structure may be formed. An investigation of the precipitate morphology, the precipitation processes and kinetics in this system is in progress.

Approach

Precipitation processes and kinetics are being determined by dynamic modulus and microhardness techniques. These are being related to precipitate structures and morphology by transmission electron microscopy and electron diffraction.

In the studies of the alloy softening effect in Fe, the approach is to measure the effect of strain rate and temperature in Fe-Mo, Fe-Ti, and Fe-Re alloys, in the solid solution range. Since a small amount of Ti scavenges interstitial atoms, measuring these properties versus Ti concentration should separate scavenging effects from intrinsic effects on the flow properties. Theoretical calculations will be made on the effect of alloying on dislocation motion.

Progress

(1) Precipitation in Ferritic Fe-base Ni-Al Alloys

Microhardness and resonant frequency data indicate a multi-stage precipitation process. Alloys quenched from 1000°C to -35°C and subsequently aged at 450 to 590°C show a small, rapid increase in micro-

hardness, which quickly levels off (Stage I). This is followed by a continually increasing hardness with aging time to a greater than 100% increase in hardness (Stages II, III). The onset of Stage II occurs at earlier times for higher aging temperatures and in alloys of higher Al concentration. Resonant frequency data indicate a third stage at long aging times. The frequency increases after having leveled-off at the end of Stage II. Transmission electron microscopy and electron diffraction show a change in morphology of the general matrix precipitate from "fiber-like" in Stage II to small, distinct particles in Stage III. An orientation relationship between precipitate and matrix exists $\langle 100 \rangle || \langle 110 \rangle$, but the exact morphology of the precipitate is as yet not clear.

(2) Iron-base Solid Solutions

The mechanical properties of polycrystalline Fe-Mo alloys up to 2 at.% Mo were investigated. The heat treatments consisted of wet hydrogen or vacuum anneals. No straightforward relation between strength and composition was found at any temperature in that increases and decreases over specific composition ranges occurred. This varied in a complex way with temperature. The strain-rate sensitivity of the flow stress ($d\tau/d \ln \dot{\gamma}$) versus temperature curves, however, all have the same form, exhibiting a maximum strain-rate sensitivity near 140 to 200°K. The temperature of the maximum decreases with increasing alloying content so that in the range from 150 to 300°K the flow stress becomes less sensitive to strain as the Mo content is increased. The influence of the wet H_2 treatments, which was designed to remove interstitial elements, decreases with increase in Mo content. Measured activation volumes seem to be consistent with an internal lattice friction mechanism as rate controlling process up to 200°K. Strain aging data seem to indicate a small interaction between molybdenum and interstitials. Foreman and Makin treated the breakaway of dislocations from a field of random pinning points using the concept of a breakaway angle. Computer calculations seem to rule out this concept for materials where the Peierls stress is controlling because the breakaway angle computes to a large value ($\sim \pi$) indicating rather straight dislocations close to the pinning points.

PUBLICATION

"Temperature Dependence of Yield Stress in Fe-1.67 at.pct. Cu and Fe-0.5 at.pct. Au," S. K. Lahiri and M. E. Fine, Metallurgical Trans., 1, 1495 (1970).

ALLOYING AND THERMAL TREATMENT OF CERAMICS

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Ph.D. Thesis Research (NDEA and AFOSR Supported)
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Ph.D. Thesis Research (Cabell Fellow and AFOSR Supported)
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This research is supported by the Air Force Office of Scientific Research.

Objective

This research is a study of precipitation and clustering and ordering in ceramics. The properties and structures of the parent and product phases and phases which show clustering or ordering are being studied. Particular attention is being given to the effects of precipitates and clustering on the mechanical and magnetic properties of ceramics.

The objectives include a determination of the effects of dispersed metallic phases of various morphologies and interparticle spacing on the fracture toughness of ceramics, ordering and clustering of the atoms in ceramic solid solutions, magnetic anisotropy properties of ceramics with precipitated ferrimagnetic phases, the limits of superparamagnetic behavior with precipitates of low anisotropy, and enhancement of the strength and/or toughness properties of ceramics by alloying and precipitation heat treatment.

Systems currently being studied are Fe-O, Mg-Fe-O, Zr-O, Co-Fe-O, Al-Ti-O, Mg-Al-O.

Approach

The approach is to obtain desired and interesting structures in ceramics by alloying and thermal treatment. The structures are studied by x-ray and electron diffraction, including diffuse scattering, and by electron and light microscopy. Considerable information about structure is also obtained from magnetic property analysis which includes measurements down to 2°K. The structures are related to other properties such as fracture, yield stress, coercive force and susceptibility in magnetic ceramics.

Fracture studies are being conducted using the double cantilever technique as well as 4 point bending of beams to determine fracture surface energy and fracture stress.

Progress

- (1) Effects of MgFe_2O_4 Precipitates on the Mechanical Properties of (Mg,Fe)O with 0 to 0.5 cat.% Fe

This research has been completed. It was reported on in last year's report. An additional result is that at small particle sizes, part of the hardening is due to the attendant increase in particle surface area when they are cut by dislocations.

- (2) Phase Decomposition in Co-Fe-O Alloys

Studies of phase decomposition within the miscibility gap in the Co_3O_4 - CoFe_2O_4 system are underway. Occurrence of spinodal decomposition, suggested in last year's report, as well as nucleation and growth have been observed. The latter occurs on aging a $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$ sample at 700°C while the former occurs on aging at 500°C. Very high intrinsic coercive forces have been observed in fully aged samples, 7500 Oe at room temperature and 22,000 Oe at 77°K (in $\text{Co}_{1.95}\text{Fe}_{1.05}\text{O}_4$). The best (BH) max observed to date is 1.2×10^6 (in $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$). This magnetic behavior is attributable to single domain particles of high anisotropy resulting from spinodal decomposition.

- (3) Fracture of Iron-Iron Oxide Composites Produced by the Decomposition of Wüstite

Wüstite hot pressed to 99.8% of theoretical density and 130 μ grain sized when aged 2½ days at 500°C contained about 12 vol.% Fe precipitated at the grain boundaries. Fracture of double-cantilever beam specimens of unaged and aged material indicated a more than doubling

of the absorbed fracture energy on aging. Aging changed the fracture mode from unstable and transgranular to stable and intergranular.

(4) Fracture Studies of Zr-ZrO₂ Mixtures

Preliminary microstructure and microhardness observations have been made on metal-excess samples prepared by cold pressing and sintering mixtures of powdered Zr and ZrO₂. The excess metal forms a continuous film between oxide grains, which have grown to ~50 μ diameter, with or without intragranular precipitated metal particles. The oxide phase is apparently in a state of compression caused by the tetragonal-monoclinic transformation on cooling, balanced by tensile stresses in the metal phase. These are eliminated by annealing just below the transformation temperature.

(5) Defect Structure of Wüstite

For some time, there has been a debate as to whether Fe_xO exists at high temperatures with a wide range of stoichiometry, or as a series of microphases with fairly narrow composition limits. Measurements of the lattice parameter at high temperatures do not indicate the presence of separate phases, indicating a single phase field of varying stoichiometry.

(6) Clustering in Mg-Fe-O Solid Solutions

Large, uniform single crystals of (Fe, Mg)O have been successfully prepared in reducing atmospheres, with Fe contents from 4 to 20 cation percent. Diffuse x-ray scattering from "alloys" with 7 and 20 cation percent indicate clustering and the presence of distortions due to the clusters. Clustering had been previously suggested from the curvature of magnetization curves at 2 to 4°K in polycrystalline specimens. However, the size of the regions, and hence the curvature of the M-H plot, is much greater in single crystals than for powder specimens. An unusual surface phase forms during heat treatment of the crystals, and at certain compositions its extra peaks are similar to those arising from spinodal decomposition. The thinness of the surface region containing this phase suggests that it is a product of a reaction with the atmosphere.

PUBLICATIONS

"Effect of Oxygen Partial Pressure on Precipitation in Titanium-Doped Aluminum Oxide," T. M. Clarke, D. L. Johnson, and M. E. Fine, J. Am. Ceram. Soc., 53, 419 (1970).

"Clustering and Precipitation in Crystalline Oxide Ceramics," Vol. IV, Advances in Materials Research, Wiley-Interscience, H. H. Herman, Editor (1970).

"Clustering and Initial Stages of Decomposition in Non-Metallic Solid Solutions," Proceedings of the Institute on the "Chemistry of Extended Defects in Non-Metallic Solids," Scottsdale, Arizona (April 1969).

INVITED TALKS

"Precipitation Processes in Ceramics and Their Effects on Electronic Properties," M. E. Fine, Keynote Speaker, Meeting of Electronics Division of the Am. Ceram. Soc., Philadelphia, Pa., May 1970.

"Kinetics and Modes of Precipitation in Ceramics," M. E. Fine, Michigan College of Mining & Technology, Dept. of Metallurgy Graduate Seminar, Houghton, Michigan, March 1970.

"Precipitation Hardening of Ceramics," M. E. Fine, Michigan College of Mining & Technology AIME Chapter, Houghton, Michigan, March 1970.

"Precipitation and Clustering Effects in Ceramics," M. E. Fine, University of Denver Colloquium, Denver, Colorado, February 1970.

"Precipitation Studies in Ceramics," M. E. Fine, North American Rockwell Science Center, Thousand Oaks, California, March 1970.

"Precipitation in Crystalline Ceramics," Illinois Institute of Technology Metallurgical Engineering Department Seminar, M. E. Fine, April 1970.

STRONG COUPLING THEORY FOR TRAPPED ELECTRONS IN SOLIDS

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Ph.D. Thesis Research

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Ph.D. Thesis Research

Objective

The primary aim of this research is to study the intra- and inter-molecular electronic transitions and transport properties of low mobility organic semiconductors.

Approach

The interaction of the electrons with the vibrations of the solid is considered in infinite order to account for local relaxation processes of the lattice. The introduction of a polaron type quasi-particle is introduced to describe radiationless transitions within molecules in a matrix. The rate for electronic transitions and the mobility is expressed in terms of a correlation function of the Kubo-type. This correlation function is analyzed for various systems and the coupling of the electron (or proton) to the vibrations is calculated. A similar approach is used to study the motion of electrons in disordered systems.

Progress

The method of canonical transformations which treats the important parts of the electron phonon interaction to infinite order has been very successful in many areas. We applied it to explain the mobility of excess protons in ice and also to calculate the excess energy dependence of non-radiative processes. The energy transfer of electronic into vibrational energy can best be studied by evaluation of the correlation function. We found that systems with many vibrational degrees of freedom, in particular solids, lead to rapid convergence of the correlation function. The application of the saddle point method and a suitable choice of the path of integration allow us to predict which modes are most effective in the process of energy transfer. We also find that interaction of the electron with quadratic terms in the nuclear displacements become quite important for several hydrocarbons. This type of interaction explains the unusual temperature dependence of some mobility data.

PUBLICATIONS

- "Theory of Electron Transport in Disordered Systems: The Nearly Free-Electron and Nearly Bound-Electron Limits," S. Fischer and S. A. Rice, J. Chem. Phys., 51, 3352 (1969).
- "SCF Calculation for Proton-Phonon Coupling in a Linear Model of Ice," J. R. Sabin, S. Fischer and G. L. Hofacker, Int'l. J. of Quantum Chemistry, III S, 257 (1969).
- "Model Approach to Nonadiabatic Reaction Processes," S. F. Fischer, G. L. Hofacker and R. Seiler, J. Chem. Phys., 51, 3951 (1969).
- "Energy Dependence of Radiationless Transitions," S. Fischer, Chem. Physics Let., 4, 333 (1969).
- "Theory of Radiationless Transitions for Large Molecules," S. Fischer and E. W. Schlag, Chem. Physics Let., 4, 393 (1969).
- "On the Sigma-Pi Separability Problem," S. Fischer, Int'l. J. of Quantum Chemistry, III S, 651 (1970).
- "Width of Zero Phonon Line for Frenkel Excitons," S. Fischer, J. of Luminescence, 1, 2, 747 (1970).
- "Spectral Behavior of Hydrogen-Bonded Systems: Quasiparticle Model," S. Fischer, M. Ratner and G. L. Hofacker, J. Chem. Phys., 52, 1934 (1970).
- "Frenkel Excitons in a Vibrating Molecular Crystal," S. Fischer and S. A. Rice, J. Chem. Phys., 52, 2089 (1970).

INVITED TALKS

- "Correlation Function Approach to Radiationless Transitions"

Illinois Institute of Technology, Chicago, Illinois, March 1970
University of Illinois, Urbana, Illinois, June 1970

- "An Analysis of the Correlation Function for a Strong Coupling Electron-Phonon System"

University of Cologne, West Germany, July 1970
Technische Hochschule München, West Germany, July 1970

ANISOTROPIC g-FACTORS OF METALS

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This research is also supported by the U. S. Atomic Energy Commission and the U. S. Air Force Office of Scientific Research.

Objective

In general the treatment of exchange enhancement has used rather idealized models in which the effect of spin-orbit coupling has been neglected and the electronic g-factor has been given a constant value of g_{eff} . The objective of this work is to carry out detailed ab initio calculations of the effective g-factors of states on all sheets of the Fermi surface of selected metals like nickel, palladium and platinum.

Approach

To determine the effect of the application of an external magnetic field B on the paramagnetic electronic states near the Fermi energy for the fcc phase of Ni, Pd and Pt metals using the SRAPW method and the combined interpolation scheme.

Progress

The Symmetrized Relativistic APW method and the combined interpolation scheme have been used to determine the effect on the energy bands of the application of an external magnetic field. The use of an outside the muffin-tin spheres potential is found to have a negligible effect on the spin-orbit splittings near the Fermi energy of the levels X_5 ($-X_5^+ \oplus X_5^-$) and L_5 ($-L_5^+ \oplus L_5^-$) consistent with the wholly d-like character of these states. The Hamiltonian we have assumed is

$$H = H_b + H_{\text{so}} + H_{\text{mag}}$$

where H_b is the band Hamiltonian, $H_{\text{so}} = \lambda \underline{L} \cdot \underline{S}$ is the spin-orbit interaction with the d spin-orbit splitting parameter λ and $H_{\text{mag}} = \mu(\underline{L} + 2\underline{S}) \cdot \underline{B}$, gives the interaction of the bands with the external magnetic field

\underline{B} (here taken along z) where μ is the Bohr magneton.

Strong spin quenching in all three systems is caused by combination of the close proximity of the dominant X_6 and L_6 (single group representation) levels to the Fermi energy and the raising of their degeneracies by the important spin-orbit interaction. Comparisons with the experimental data, in particular static susceptibility and dHvA orbital g-factors are encouraging.

PUBLICATION

"Anisotropic g-Factors of Nickel, Palladium, and Platinum," A. J. Freeman, F. M. Mueller, and D. D. Koelling, J. Appl. Phys., 41, 1229 (1970).

ELECTRONIC BAND STRUCTURE AND PROPERTIES OF METALS AND ALLOYS

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This research is also supported by the U.S. Atomic Energy Commission and the U.S. Air Force Office of Scientific Research.

Objective

To determine the electronic band structure of metals and alloys and to predict the electric, magnetic and optical properties.

Approach

To carry out detailed calculations of the band structure, density of states and Fermi surface of metals and alloys using the first principles Symmetrized Relativistic APW method and the semi-empirical combined interpolation scheme of Mueller.

Progress

1. A detailed investigation of the electronic structure of palladium was carried out (in collaboration with J. O. Dimmock, Lincoln Laboratory, M.I.T., and A. M. Furdyna, Francis Bitter National Magnet Laboratory, M.I.T.) in terms of two different band models: (1) ab initio calculations using the APW method and (2) relativistically augmented calculations using the combined interpolation scheme. The width and position of the d-band complex are found to be particularly sensitive features of the electronic structure of palladium. Highly accurate density of states histogram estimates for the first and second derivatives of the density of states at the Fermi energy are derived. In addition, detailed comparisons were made with Fermi surface, static susceptibility, and specific heat experimental results. Estimates for the effects of many-body enhancements suggest that paramagnons raise the effective mass at the Fermi energy by only about 41%. Due to the strong s-d hybridization in palladium the Fermi surface is made up almost entirely of d-like states. Because the Fermi energy in palladium falls near the strongly spin-orbit split levels at X and L, spin quenching reduces the effective g factor at the Fermi energy from 2 to about 1.65. This increases an estimate of the

effective Stoner enhancement factor from 10 to about 15. The use of a parametrized phase-shift representation in order to obtain improved fits to accurate experimental data is sketched.

2. The energy band structure of the actinide metals and their compounds is being studied by means of the SRAPW method. Calculations were done for uranium metal in its low temperature (orthorhombic) and high temperature (b.c.c.) forms. As starting potential we use the superposition of atomic potentials calculated by Lieberman, Waber and Cromer, using the relativistic Hartree-Fock-Slater method. Unlike the case of the rare-earth metals in which the 4f bands are well below the (5d, 6s) conduction bands, the 5f bands, which are responsible for many of the properties of the actinide metals (and the magnetic properties of their compounds), are strongly admixed into the (6d, 7s) conduction bands. A number of properties of these metals are being investigated using our calculated bands and density of states.

3. The low Z end of the 3d transition metals display a number of interesting properties not characteristic of (and different from) the rest of the group. We have studied Sc metal as representative of this group in order to understand the generalized magnetic susceptibility, electronic specific heat, photoemission data, Fermi surface and transport properties. Of particular interest is the role of dynamic interactions (electron-electron, electron-phonon, and the newly proposed electron-antiparamagnon) on the observed properties of the metal and its dilute alloys. To this end we have done a complete APW calculation of the electronic band structure (four of the bands having been previously determined by Fleming and Loucks) of hcp Sc metal using the Symmetrized Relativistic APW method for potentials made up from two different atomic configurations ($3d^{14}s^2$ and $3d^{24}s^1$) each with variable Slater exchange coefficients. From these bands and using the QUAD scheme (modified for hexagonal structures), a full density of states is being obtained and an accurate Fermi surface determined.

4. In collaboration with S. G. Das we have considered the effect of up to 100 kilobars of pressure on the Fermi surface of palladium for two experimental situations: de Haas-van Alphen extremal cross-sectional areas and position annihilation spectra as measured by point and slit detectors for single and polycrystalline samples. Initially the energy levels at high symmetry points were calculated using the SRAPW method and potentials derived from a single $4d^{10}5s^0$ atomic configuration for seven different lattice spacings. These were used to fit parameters for the combined interpolation scheme, from which QUAD produced densities of states, and FORFIT Fermi surface contours were constructed. The position annihilation spectra were calculated using the POSGO technique. Comparisons with the experimental data will be made where appropriate.

PUBLICATION

"Electronic Structure of Palladium," F. M. Mueller, A. J. Freeman, J. O. Dimmock and A. M. Furdyna, Phys. Rev., 1B, 461 (1970).

HIGH-FIELD STUDIES OF BAND FERROMAGNETISM IN Fe AND Ni

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Objective

Two models for ferromagnetism have been discussed for many years -- the localized model and the band or collective (itinerant) electron model. Although differences are predicted by the collective models, there are few experiments which permit a clear distinction between the localized and the itinerant models. These experiments are difficult to perform with sufficient resolution. The objective of this work is to study the high field magnetic susceptibility in Fe and Ni in order to relate the band structure of iron and nickel and band models of ferromagnetism.

Approach

To measure the high field magnetic susceptibility of Fe and Ni at 4.2, 77 and 300°K and the hyperfine field at the ^{57}Fe nucleus in Fe at 4.2°K subjected to high magnetic fields. To relate these experimental results to the band theory of magnetism.

Progress

The Mössbauer effect was employed to measure the change in the hyperfine field H_N at the ^{57}Fe nucleus with application of an external field. Assuming H_N to be proportional to the bulk magnetization a

microscopic equivalent to χ_{HF} was obtained. The high-field data may be used alternatively to determine the nuclear g factor. Macroscopic differential magnetic moment measurements were done up to 150 kG. We find $\chi_{HF} = 4.3 \times 10^{-5}$ emu/cc for Fe and 1.7×10^{-5} emu/cc for Ni at 4.2°K, where χ_{HF} is averaged from 50-150 kG. The interpretation of these low-temperature data (when reasonable estimates of Van Vleck susceptibility are made) indicates holes in both spin bands of Fe and a full band of one spin in Ni, in agreement with the accepted band theory picture for these metals and with recent spin-polarized and pseudopotential band calculations for magnetic Fe and Ni. The differential magnetic moment measurements at higher temperatures are in reasonable agreement with predictions of spin-wave theory.

PUBLICATION

"High-Field Studies of Band Ferromagnetism in Fe and Ni by Mössbauer and Magnetic Moment Measurements," S. Foner, A. J. Freeman, N. A. Blum, R. B. Frankel, E. J. McNiff, Jr., and H. C. Praddaude, Phys. Rev., 181, 863 (1969).

THEORY OF COVALENCY: SPIN DENSITIES AND NEUTRON MAGNETIC SCATTERING

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This research is partially supported by the Advanced Research Projects Agency and the U.S. Air Force Office of Scientific Research.

Objective

The objective of this study is to develop a theory of covalency for molecular complexes containing transition metal and rare-earth ions. Accurate charge and spin density distributions in magnetic insulating systems will be determined and both direct and super-exchange mechanisms thought to be responsible for the observed magnetic behavior in ferromagnetic and anti-ferromagnetic systems will be studied theoretically.

Approach

The unrestricted Hartree-Fock molecular orbital and configuration interaction methods are developed for clusters of atoms like MnF_6^{4-} in which all electrons are treated explicitly by evaluating the Fock matrix directly, using Monte-Carlo integration techniques.

Progress

Self-consistent Hartree-Fock molecular orbital calculations, including all electrons, for the $(\text{MnF}_6)^{4-}$ cluster, as in KMnF_3 , yielded an explanation of the puzzling neutron scattering results which were in conflict with the simple LCAO theory. The calculations show clearly that the open e_g shell in $(\text{MnF}_6)^{4-}$ has a considerable admixture of ligand density, as is the case in $(\text{NiF}_6)^{4-}$ previously studied; however, the open t_{2g} shell orbitals which point between the ligands have expanded in order to share more fully in the bonding region between ligand "p π " orbitals. Qualitatively, it appears as if the metal 3d- t_{2g} orbital had slightly expanded, compared to the free ion, accounting for the experimental observations. These results strengthen the claim that the molecular orbital formulation of covalent bonding theory can give an accurate description of the transition metal salts. Further work is in progress to improve the efficiency of the computer codes, and to resolve the optical and magnetic transitions to several excited states.

The effects of covalent bonding on neutron magnetic scattering factors were studied further by comparing results calculated for the isolated Sc^{2+} ion with those obtained for diatomic ion $(\text{Sc}_2)^{4+}$, and with the linear molecule $(\text{Sc}_2\text{F})^{3+}$. These comparisons are particularly useful in determining the "shifts" in scattering amplitude caused by bonding. Both ferromagnetic ($M_s=1$) and antiferromagnetic ($M_s=0$) states were studied, using a point ion approximation for the metal cores; some preliminary work has been done to study the (rather weak) effects of core polarization on the scattering.

The shortcomings of Hartree-Fock virtual (unoccupied) orbitals in describing the excited states of atomic and molecular systems have been known for a long time. In an attempt to develop methods which produce suitable excited state basis functions, we have implemented the Hartree-Fock-Slater statistical exchange model for molecules, using the same numerical scheme applied successfully to solids. Preliminary results have been obtained for several hydrocarbons and the $(\text{MnF}_6)^{4-}$ complex.

PUBLICATIONS

- "Covalency, Spin Densities, and Neutron Magnetic Scattering," D. E. Ellis and A. J. Freeman, J. Appl. Phys., 41, 937 (1970).
- "Covalent Bonding and the Neutron Magnetic Form Factor of the Mn^{2+} Ion," A. J. Freeman and D. E. Ellis, Phys. Rev. Letters, 24, 516 (1970).

INVITED TALKS

- "Covalency, Spin Density, and Magnetic Behavior of Rare Earth Ion Complexes," 1970 International Conference on Magnetism, Grenoble, France, September 1970.
- "Covalent Bonding and Spin Density," Third Sagamore Conference on Charge and Spin Density, Assois, France, September 1970.

THEORY OF ELECTRONIC BAND STRUCTURE OF METALS

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This research is also supported by the U.S. Air Force Office of Scientific Research.

Objective

To develop further theoretical methods for obtaining accurate electronic energy bands in solids in order to determine their electronic and optical properties.

Approach

To investigate the validity of various approximations for calculating electronic band structures using the Symmetrized Relativistic Augmented Plane Wave (SRAPW) method. To test out ideas, we use the unique programs of Dr. Koelling which are especially valuable for calculations on high atomic numbers.

Progress

1. We have developed the symmetrized formulation of the relativistic augmented plane wave method (SRAPW). This method is a variation of the APW technique which takes account of the relativistic effects by using the Dirac equation near the atoms and the non-relativistic approximation when far from the atoms. The resulting simplification of being able to talk about Pauli spinors instead of the full 4-component wave functions is of great value when dealing with the already complicated magnetic materials. The SRAPW method has been applied to gray tin to test a number of potential approximations, including nonself-consistency and the treatment of exchange as well as the various features of the muffin-tin approximation to the model potential. The results show that, of the terms left out of the muffin-tin approximation to the model potential, the additional warping of the potential outside the muffin-tin spheres has the most significant effect.

2. We have also developed an alternative approach to the APW method obtained by focusing on the continuity conditions at the APW sphere radius. It has in common with the APW method, as well as the

OPW methods proposed, the use of the energy-variational formalism. Therefore, what is actually being sought is a prescription for setting up a set of basis functions in which to expand the trial function. Our prescription is based on the (truncated) expansion of the radial function inside the APW spheres in the two sets of functions u_n^l and v_μ^l defined by being a solution to the radial equation and satisfying the boundary conditions:

$$u_n^l(R_s) = 0; \quad \frac{d}{dr} u_n^l(R_s) \equiv 1; \quad v_\mu^l(R_s) \equiv 1; \quad \frac{d}{dr} v_\mu^l(R_s) \equiv 0.$$

Obviously, the matching of the radial function at the APW sphere boundary is easily done using these functions for each l . We have developed a formalism required to apply this procedure to a muffin-tin potential and have performed the small modifications necessary to apply the method to non-muffin-tin potentials. A test application of the method to the Chodorow potential for copper has been made with good success. Further, information on the applicability of pseudo-potentials has been obtained.

3. Many calculations of the electronic band structure of materials have utilized the muffin-tin approximation to the one-electron potential. First introduced by J. C. Slater in his 1937 paper on the Augmented Plane Wave (APW) method, this approximation offers several simplifying features in carrying out the numerical calculations. The crystal potential, which is constructed by taking a superposition of spherically averaged free atom charge densities from the neighboring atoms, is made spherically symmetric within a sphere about each atomic site. For those metals which have many tightly bound core electrons and only a few, nearly-free-conduction electrons, viz. the simple and noble metals, the muffin-tin approximation is rather inadequate, and the corrections introduced by the nonflat potential outside the muffin-tin spheres can cause substantial shifts in selected energy levels. For the intermediate case of the transition and actinide metals, the effect of the muffin tin approximation has not been studied and is not well known. We have included the variations of the potential outside the muffin-tin sphere into relativistic APW calculations and have shown for the case of transition and actinide metals--specifically, fcc palladium, fcc platinum and bcc uranium--the resultant corrections which are introduced into the calculated energy bands. These generally neglected contributions induce average energy shifts of the order of 0.005 to 0.010 Ryd. The high band mass of these transition metals combined with such shifts can cause errors of the order of 5 percent in predicting the Fermi radii. The splitting of the spin-orbit doublets is found to be insensitive to the inclusion of the outside of the muffin-tin potential. By augmenting a phase shift parameter set by 2 or 3 effective pseudopotential coefficients which represent the effect of the weak added potential an ab initio band structure may be used to fit accurate experimental data.

PUBLICATIONS

- "The Symmetrized Relativistic APW Method: Gray Tin and the Warped Muffin Tin Potential," Dale D. Koelling, Phys. Rev., 188, 1049 (1969).
- "An Alternative APW Technique: Theory and Application to Copper," Dale D. Koelling, Phys. Rev., 2B, 290 (1970).
- "Shifts in the Electronic Band Structure of Metals Due to Non-Muffin Tin Potentials," A. J. Freeman, F. M. Mueller and D. D. Koelling, Phys. Rev., 1B, 1318 (1970).
- "On the Success of Pseudopotential Methods," D. D. Koelling, Physics Letters, 32A, 277 (1970).

HIGH TEMPERATURE MATERIALS

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This research is also partially supported by the National Institutes of Health.

Objective

The present research program is directed towards determining the effects of various alloying elements on the allotropic transformation of cobalt and cobalt alloys. The information obtained on the stability of various phases, the kinetics and mechanisms of the phase transformations and the morphology of the resulting transformation products is being used in conjunction with mechanical property data to determine the optimum structures for desired properties. In addition, quantitative x-ray diffraction techniques are being applied to multiphase alloys to evaluate the accuracy of volume fraction determinations when preferred orientation exists.

Approach

The main tools being used in the investigation of kinetics and mechanism of the phase transformations in cobalt base alloys are: optical and electron microscopy, quantitative x-ray diffraction and dilatometric techniques. Mechanical property data are being obtained from tensile and hardness tests. Hot rolled sheet specimens of Co-W alloys containing 30 or 35 wt.% W are being utilized as the starting materials for the electron microscopy and mechanical property studies.

The quantitative x-ray diffraction studies are being conducted on Fe-Ni and Fe-C martensitic steels containing various percentages of retained austenite. An x-ray diffractometer equipped with an incident beam monochromator and a sample spinner is being utilized to collect the necessary intensity data.

Progress

Electron microscopy observations of the Co-35 wt.% W alloy quenched from above 1200°C showed a single phase fcc material containing numerous stacking faults which is in agreement with previous x-ray data. Upon aging for short periods of time (< 1 hr) at 800°C, a temperature which is below the peritectoid reaction isotherm, additional diffuse diffraction spots are observed on the electron diffraction pattern which can be attributed to an α -Co₃W precipitate. The α -Co₃W precipitate is an ordering of the Co and W atoms on the fcc matrix lattice to give an ordered structure similar to Cu₃Au. At present, it is believed that the α -Co₃W precipitates are completely coherent with the matrix fcc material. After approximately 1 hr of aging at 800°C, regions of very high stacking fault density appear. Upon further aging, small regions of hcp matrix material are observed to form. At the same time diffraction effects which are attributable to the hexagonal β -Co₃W are observed. Prolonged aging experiments are being conducted to determine the morphology relationships and reaction mechanisms leading to the final equilibrium products.

Tensile tests on solution treated Co-30 wt.% W alloys have shown approximately 15% elongation up to fracture with little or no necking prior to fracture. Examination of the microstructure after deformation shows numerous markings and striations within grains which are believed to be the result of a deformation induced transformation of fcc material to hcp material. X-ray diffraction studies tend to confirm this hypothesis. Further studies on these alloys after various aging treatments are planned.

Quantitative x-ray diffraction techniques developed previously for studies of aging in Co-WC alloys are being applied to Fe-Ni and Fe-C martensitic steels to determine the percentage of retained austenite when preferred orientation is present. By utilizing a sample spinner, reproducible intensity ratios have been obtained on all samples. Further, the percentages of retained austenite determined from the x-ray diffraction data are in agreement with the values obtained by quantitative optical metallography on the Fe-C martensites.

PUBLICATIONS

"Open-Circuit Potentials and Microstructure of Some Binary Co-Cr Alloys,"
E. J. Freise, A. Acharya and E. Greener, Cobalt, 47, 75 (1970).

STRUCTURE AND PROPERTIES OF INTERMETALLIC COMPOUNDS

E. J. Preise

Associate Professor, Department of Materials Science

E. Kraft

Ph.D. Thesis Research (Completed)

H. Gasmueck

M.S. Thesis Research

This research is supported by the Office of Naval Research.

Objective

The primary goal of this research is to determine the factors governing the ductility of intermetallic compounds. Relationships between crystal structure, bonding and defect structure and the presence or absence of ductility in intermetallic compounds is being sought.

Approach

Simple hardness tests have been used to determine the primary modes of deformation in NiSb. Single crystals grown by direct solidification have been utilized for these tests to permit identification of the slip planes. Hot hardness tests have been used to study the effects of the defect structure on the deformation behavior.

Work has also continued on attempting to grow single crystals of refractory metal carbides and borides. Electrolytic deposition from a fused salt bath is being examined to determine the suitability for growth of single crystals and the conditions under which maximum growth will occur.

Progress

Analysis of the hardness tests on NiSb as a function of composition and temperature has been completed. On the metal rich side of stoichiometry, the defect structure consists of excess nickel atoms located in the trigonal voids of the hcp antimony sublattice. On the metal deficit side of stoichiometry, the defect structure consists of vacancies on the nickel sublattice. Both defect structures lead to higher hardness values at room temperature with increasing deviations from stoichiometry. The rate of hardness increase is greater for the nickel interstitials than for the vacancies. At elevated temperatures, the hardness differences become less pronounced. At 800°C all compounds tested exhibit approximately the same hardness value indicating that thermally introduced defects probably override any defects introduced by deviations from stoichiometry.

In plots of the log of the hardness vs testing temperature, two linear regions were observed for all crystal orientations and compositions tested. In the high temperature region, the hardness value was observed to be a function of loading rate and the time that the sample was subjected to full load on the indenter. This is taken as an indication that the high temperature deformation is a diffusion controlled process. Furthermore, the slip line patterns around hardness indentations change from very straight to markedly curved patterns as the testing temperature is raised. In the low temperature testing range deformation occurs primarily by slip on the $\{10\bar{1}0\}$ planes. Slip is also observed to occur on the $\{10\bar{1}1\}$ and $\{0002\}$ planes. All three systems were predicted to be potential slip systems on the basis of a hard sphere model for deformation in the NiSb system.

Electrolytic deposition from a fused salt bath has been attempted to obtain crystals of MoB_2 . The bath composition consists of borax, sodium fluoride and molybdenum trioxide. Preliminary results from the initial runs indicate a deposit on the electrodes of a bluish-black crystalline-appearing material which has been tentatively identified as MoB_2 .

ELECTRICAL CONDUCTION IN FERROMAGNETIC METAL OXIDE JUNCTIONS

R. Frerichs

Professor, Department of Electrical Engineering

R. K. Smeltzer

Ph.D. Thesis Research (Completed)

Objective

The purpose of this study is to determine the electrical conduction mechanisms in thin film metal-oxide-metal junctions using the three common ferromagnetic metals and their oxides. The important parameters of the junctions are the metal-oxide barrier heights and the effective junction thickness.

Approach

Thin film junctions of the type $\text{Ni-NiO}_x\text{-M}$, Co-CoO-Pb , and $\text{Fe-FeO}_2\text{-Pb}$, where M is Pb, Ni or Ag, have been made. Conditions were established to thermally grow the oxide films. The oxide layers varied in thickness from the thinnest solid layer to about 100 Angstroms. Lead (Pb) was used as the overlayer metal for most of the junctions because it is a superconductor with a transition temperature above 4.2°K. By simply dipping the junctions into liquid He the presence of the superconducting Giaever characteristic can be used to establish electron tunneling conductivity. The dc conductivity of the junctions was studied as a function of the measurement temperature and the junction thickness. The final analysis of the results was made by comparing the data with the characteristics of the possible conduction mechanisms in metal-oxide-metal junctions.

Progress

This research is the first work investigating in detail the electrical conduction in thin film metal-oxide-metal junctions using nickel oxide grown on nickel as the base layers. A technique was found to grow reproducible and controllable oxide layers. Quantum mechanical tunneling is the dominate conduction mechanism at low temperature; near room temperature, Schottky thermionic emission dominates. The effective junction thickness determines at what temperature the conductivity changes from tunneling to Schottky emission. The barrier heights in the nickel oxide junctions are 0.2 eV. It appears that there are broad transition regions at the metal-oxide interfaces, so that the barriers cannot be localized. Junctions with oxides of iron and cobalt are similar to the nickel oxide junctions.

ELECTRICAL CONDUCTION IN INHOMOGENEOUS SEMICONDUCTORS

C. Goldberg

Professor, Department of Electrical Engineering

H. Yamasaki

Ph.D. Thesis Research (Completed)

Objective

The main objective of this program is to determine the factors that influence electrical current in inhomogeneous semiconductors. Of particular interest are those regions where high electric fields are present in equilibrium and the inhomogeneous regions which exist when the current density is large. The results are directly applicable to the determination of what occurs within the space charge region of a p-n junction and of a ohmic contact.

Approach

The electric field, current, carrier concentrations and carrier temperatures in inhomogeneous regions can be determined by solving the appropriate set of seven simultaneous, non-linear differential equations. Analytical solutions for this set of equations can be obtained for certain limiting conditions but, in general, numerical methods must be used.

Progress

The equations have been solved for n^+-n junctions and for symmetrical p-n junctions. Although some approximations were made, all major physical phenomena are included. For the n^+-n junction it has been shown that a one-carrier model (i.e., holes are ignored) is satisfactory at low current levels but at high current levels the effect of minority carriers becomes quite pronounced and the holes must be considered. This work can be compared to previous work by considering the limiting cases of very small energy relaxation times or minority carrier lifetimes. In these limiting cases agreement with the literature is obtained but the results obtained with more realistic values for these parameters indicate the importance of solving the problem accurately. It has been shown, for example, that at an "ohmic contact" the carrier temperatures can deviate significantly from the equilibrium values. Thus, although assuming an equilibrium value for the carrier temperature at a contact is very convenient when discussing charge transport, this assumption is seriously in error and undoubtedly leads to the misinterpretation of what is occurring in the crystal.

PUBLICATIONS

"Electric Currents in a Semiconductor Space-Charge Region," C. Goldberg, J. Appl. Phys., 40, 4612 (1969).

RADIATION BEHAVIOR OF POLYMERS

W. W. Graessley

Professor, Departments of Chemical Engineering and Materials
Science

K. Yonetani

Ph.D. Thesis Research (ARPA Supported)

Objective

High energy radiation causes crosslinking and chain scission in solid polymers. Irregularities in the molecules, such as end groups and branch points, appear to contribute far in excess of what one would expect from their concentrations. How this happens and how radiation sensitivity can be conferred, enhanced or suppressed by incorporation of the proper chemical structures in the molecules is the subject of this study.

Approach

Linear polyvinyl acetate is crosslinked by gamma irradiation in vacuum. Polymers can be prepared with small but controllable amounts of long chain branching (0-2 branch points per molecule or 0 to 0.4 branch points per 1000 repeating units) in the chains. Copolymers of vinyl acetate (VA) with traces of isopropenyl acetate (IPA) or 1-propenyl acetate (NPA) can be prepared to contain known numbers of small branches (α -methyl and β -methyl groups). Effects of these structures on radiation response are being studied by a variety of techniques: molecular weight measurements, determinations of gel fraction, gas evolution studies, and trapped free radical measurements.

Progress

Molecular weight measurements in the pre-gel region confirm a rapid and preferential chain scission at approximately 15% of the long chain branch points, the remainder appearing to be no more susceptible to radiation than ordinary repeating units. According to structural studies on the parent polymer, this is approximately the fraction of branching that occurs through the α -hydrogen position in the vinyl acetate mer. The VA-IPA copolymers, containing α -methyl groups instead of long chain branches, show enhanced free-radical formation and cross-linking rates at low methyl group concentrations (1 to 20 methyl groups per 1000 mer units), a result again consistent with a preferential scission at α -branches. Electron spin resonance spectra indicate that the total trapped radical concentrations are the same in the homopolymers and copolymers but that the chemical structure of the radicals

is different. Differences in the molecular weight changes produced by annealing confirms this structural difference. Studies on VA-NPA copolymers indicate, however, that isolated β -methyl groups are no more sensitive to radiation than homopolymer units. Results on mixtures of homopolymer and α -methyl copolymers suggest strongly that energy is quite mobile over large distances within polymer chains but does not pass easily from one chain to another.

PUBLICATIONS

"Radiation Effects in Homopolymers and Dilute Copolymers of Vinyl Acetate," W. W. Graessley and K. Yonetani, *Polymer (London)*, 11, 222 (1970).

POLYMERIZATION AND STRUCTURE OF BRANCHED POLYMERS

W. W. Graessley
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Science

A. Chatterjee
M.S. Thesis Research (ARPA Supported)

A. Daniil (Directed Jointly with Professor J. Dranoff)
Ph.D. Thesis Research (NSF Supported)

J. Dhuey
Ph.D. Thesis Research (Cabell Fellowship)

M. Farahat
M.S. Thesis Research (Completed)

J. Kathju
M.S. Thesis Research (NSF Supported) (Completed)

This research is principally supported by the National Science
Foundation.

Objective

Branching occurs in free radical polymerizations by reactions between growing radicals and already formed polymer molecules. Vinyl acetate polymerization is a convenient and representative system in which to study the effects on structure and molecular weight distribution.

Approach

Vinyl acetate is polymerized to various extents of conversion. Molecular weights are measured by osmometry and light scattering and used to establish the kinetic parameters of the system. Intrinsic viscosity, gel permeation chromatography, and ultracentrifugation provide additional information on structure and distribution.

Progress

A laboratory scale stirred tank reactor was constructed to polymerize vinyl acetate continuously. As predicted, the distribution at all conversions is broader than in batch polymerizations, and the branching density is higher. Earlier difficulties due to inhibiting impurities have been overcome by scrupulous purification of monomer, avoidance of contact with oxygen during polymerization and pre-polymerization of the feed.

Attempts to correct the gel permeation chromatograph (GPC) traces for axial dispersion have been unsuccessful. Characterization of molecular weight distribution by GPC is now being done under conditions which minimize such dispersion effects, and equipment modification to accomplish this is being made. Complementary studies on the ultracentrifuge are in progress.

PUBLICATIONS

- "Molecular Weight Distribution at High Conversions in Free Radical Polymers," W. W. Graessley, W. C. Uy, and A. Gandhi, I & EC Fundamentals, 8, 696 (1969).
- "Studies of Branching in Polyvinyl Acetate," W. W. Graessley, R. D. Hartung, and W. C. Uy, J. Polymer Sci. Part A-2, 7, 1919 (1969).
- "Molecular Weight Distribution in Branched Polymers," W. W. Graessley, O. Saito, and K. Nagasubramanian, J. Polymer Sci. Part A-2, 7, 1937 (1969).
- "Intrinsic Viscosity in Branched Free-Radical Polymers," W. W. Graessley, K. Nagasubramanian, and O. Saito, J. Polymer Sci. Part A-2, 7, 1955 (1969).

INVITED TALKS

- "Polymerization Reactor Design and Polymer Properties," AIChE Symposium (Chicago Section), April 1970.

RHEOLOGY OF POLYMER SYSTEMS

W. W. Graessley
Professor, Departments of Chemical Engineering and Materials
Science

R. Crawley
M.S. Thesis Research (NSF and ARPA Support)

J. Garvin
M.S. Thesis Research (NSF Support)

W. Uy
Ph.D. Thesis Research (Completed) (PRF Support)

This research is principally supported by the Petroleum Research Fund and the National Science Foundation.

Objective

The work aims to relate viscous and elastic properties of polymers to molecular parameters such as molecular weight, molecular weight distribution and degree of chain branching.

Approach

Polymers with accurately known structures are prepared, and their flow properties are studied. Both concentrated solutions (15 to 55%) and undiluted polymers are used; the instruments are a plate-cone rheogoniometer and a capillary extrusion rheometer. Theoretical studies of relaxation time distributions in entangling systems are also in progress.

Progress

Recently completed measurements on a series of linear polyvinyl acetate samples have confirmed the generality of relations (described in earlier Annual Reports) between the viscosity time constant, normal stresses, molecular weight distribution, and entanglement density in polystyrene systems (described in earlier annual reports). These results on steady shearing flows have prompted a continuation involving transient flows, especially the build-up of stresses at the initial stages of flow and stress decay when the flow ceases. Current work involves modification of the rheogoniometer, mainly replacement of the slowly responding transducer detectors by piezoelectric crystals.

Additional theoretical studies are underway to clarify entangling interactions in polymers by means of computer simulation. The equilibrium interactions between chain pairs are presently being characterized; time dependent effects will be studied in the coming months.

PUBLICATIONS

"Effect of Molecular Weight Distribution on the Shear Dependence of Viscosity in Polymer Systems," W. W. Graessley and L. Segal, AIChE Journal, 16, 261 (1970).

INVITED TALKS

"Rheology of Polymer Systems"

Bell Telephone Laboratories, Murray Hill, N. J., December 1969.

American Chemical Society (Washington Section), Washington, D.C., December 1969.

University of Wisconsin, Madison, Wisconsin, April 1970.

DuPont de Nemours and Company (Fabric and Finishes Department), Flint, Michigan, April 1970.

Program Design, Inc., Cherry Hill, N. J., June 1970.

Gordon Research Conference on Polymer Physics, Andover, New Hampshire, July 1970.

QUANTITATIVE DETERMINATION OF MICROSTRUCTURES

J. E. Hilliard

Professor, Department of Materials Science and
Engineering Science

Objective

The purpose of this research is to find means of specifying and estimating the three-dimensional properties of microstructures. The primary emphasis is on the evaluation of sampling errors and the development of optimum procedures for the analyses.

Approach

The approach involves the use of geometrical probability and statistics. Where necessary, experimental tests are made of the theoretical treatment.

Progress

A study is presently being made on the quantitative analysis of scanning electron micrographs. The procedures involved differ greatly from those used in the analysis of optical or electron transmission micrographs.

PUBLICATIONS

"Optimum Procedures for Determining Spatial Parameters Related to Mechanical Properties," in Quantitative Relation Between Properties and Microstructure (Ed. D. G. Brandon and A. Rosen) Israel Universities Press, Jerusalem (1969) pp. 3-15.

"Optimum Procedures for Determining Ultrafine Grain Sizes," J. E. Hilliard, J. B. Cohen, and W. M. Paulson, in Ultrafine Grain Ceramics, Syracuse University Press, Syracuse, New York (1970) pp. 73-98.

THERMODYNAMICS AND KINETICS IN SOLID SOLUTIONS

J. E. Hilliard

Professor, Department of Materials Science and
Engineering Science

W. Paulson

Ph.D. Thesis Research

M. Yang

Ph.D. Thesis Research

H. Yamauchi

Ph.D. Thesis Research

D. Spreng

Ph.D. Thesis Research

P. Rexford

M.S. Thesis Research

This research is supported by the Advanced Research Projects Agency, the National Science Foundation, the Army Research Office - Durham, and the Copper Research Institute.

Objective

The objectives are to study: (1) The effect of extreme conditions on diffusion; (2) The mechanism of spinodal decomposition; (3) The properties of solid solutions related to interatomic binding energies.

Approach

- (1) Use of vapor-deposited specimens containing short wavelength (7-40Å units) composition modulations for diffusion measurements.
- (2) Use of x-ray diffraction and electrical resistance measurements to follow the growth or decay of the modulations.

Progress

(1) An investigation in collaboration with Professor J. W. Kauffman has been completed on the effect of electron irradiation on diffusion in gold-silver alloys at liquid nitrogen temperature. For an electron flux of $2 \mu\text{A cm}^{-2}$ with an electron energy of 2.0 MeV the effective diffusivity was found to be $1.5 \times 10^{-22} \text{ cm}^2 \text{ sec}^{-1}$. All the evidence suggests that this mixing during irradiation was due to the migration of interstitialcies. It was also found that the diffusivity was directly proportional to the

beam current and that, over the range of electron energy studied (1.0-2.2 MeV), the diffusivity increased with increasing energy. On heating up to room temperature after irradiation, further mixing occurred at approximately -50°C. This is attributed to the migration of vacancies that were formed during irradiation but did not become mobile until the higher temperature was reached.

(2) It has been established that at low temperatures (less than approximately 300°C) gold-nickel alloys can decompose spinodally. For decomposition in the $\langle 111 \rangle$ directions the maximum in the spinodal was found to be 300°C, which is considerably higher than hitherto expected. The kinetics of decomposition and the dependence on the wavelength of the modulation was in quantitative accord with Cahn's theory of this transformation.

PUBLICATION

"Spinodal Decomposition" in Phase Transformations (Ed. by H. I. Aaronson, American Society for Metals, Metals Park, Ohio (1970)) pp. 497-560.

INVITED TALKS

"Diffusion in Thin Films," AIME Symposium, October 1969.

"The Gradient Energy Contribution to Diffusion," Pratt and Whitney Aircraft Advanced Materials Research and Development Laboratory, February 1970.

"Diffusion in Thin Films," IBM Research Center, March 1970.

"Effect of Coherency Strains on Diffusion," Kennecott Copper Corporation, Ledgemont Laboratory, March 1970.

ULTRA THIN CRYSTAL NUCLEATION AND GROWTH

R. L. Hines

Professor, Department of Physics

W. Krakow

Ph.D. Thesis Research (Completed)

Objective

This project uses vacuum evaporation of materials to investigate the growth of thin crystals and to determine the factors that limit the thickness and purity of the crystals that can be prepared.

Approach

The material under consideration, e.g., gold, is evaporated in an ultra-thin high vacuum unit onto a heated crystal such as rocksalt or mica. After the desired amount of material has been deposited, the sample is removed from the vacuum system and is examined in an electron microscope. Depending on the experiment, the film is either removed from the supporting crystal or else the supporting crystal is thinned.

Progress

Gold crystals with many good twin boundaries have been produced by vacuum evaporation. The thickness fringes that are seen in the twin boundaries in dark field observation have been used to obtain experimental values for the absorption coefficients and lattice potentials for gold. Measurements are made with several different objective apertures to determine the objective aperture dependence. The interpretation of the fringes is complicated by many-beam effects and the uncertainty in the exact value of the deviation parameter. Many-beam calculations have shown that the first few thickness fringes at twin boundaries are changed in periodicity and attenuated. Good agreement is obtained between the experimental and theoretical results.

PUBLICATIONS

"Nucleation of Gold on Muscovite Mica," W. L. Morris and R. L. Hines, J. Appl. Phys. 41, 2231 (1970).

RADIATION EFFECTS ON ION BOMBARDMENT

R. L. Hines
Professor, Department of Physics

D. Weber
Ph.D. Thesis Research (Completed)

This research is supported by the Atomic Energy Commission.

Objective

This project uses ion bombardment to investigate the ranges of Kev atoms in crystals, the creation and annealing of imperfections produced by the Kev atoms, and the effect of the imperfections on the physical properties of materials.

Approach

The ion beams are formed in a low-pressure source, magnetically analyzed to select the desired mass, and then accelerated to the desired energy. At the target region the beam is sufficiently intense to create radiation damage at a rate one million times greater than is achieved in a nuclear reactor. For range and channeling measurements, the transmission of the ions through thin crystal foils mounted on a goniometer is investigated as a function of crystallographic orientation of the foil with respect to the incident beam. The imperfections produced by the ion bombardment are examined with an electron microscope.

Progress

Numerous bombardments of high-perfection gold foils have been carried out as a function of ion energy between 3 and 40 Kev. The foils orientation during bombardment is set to minimize channeling effects. Good reproducibility is now obtained between different foils. Structure is frequently seen within the imperfect regions produced by the ion impacts. The ratio of damage clusters per ion impact is observed to have a threshold near 4 Kev, increase to 0.5 at 10 Kev, and reaches a saturation value of unity near 20 Kev. All of the bombardments are done with a sufficiently low ion flux so that there is little overlap between individual ion impacts.

THEORETICAL STUDIES OF PROTON TRANSFER MECHANISMS IN HYDROGEN BONDED SOLIDS

G. L. Hofacker*

Associate Professor, Department of Chemistry

R. Rosenstein

Ph.D. Thesis Research (Completed)

Objective

The main objective of this research is to study the protonic motion in hydrogen bonded solids and analyze the effects of lattice vibrations on the transfer rate.

Approach

The rate for proton transfer can be expressed in terms of a correlation function. An analysis of the correlation function is particularly practicable if the dynamical interaction with the lattice vibrations plays an important role in the transfer process.

Progress

The time dependent correlation function has been evaluated in the classical and quantum mechanical limits. A short time expansion leads to the well-known motion over the barrier as is given in the Eyring type formulas. A local relaxation of the lattice leads to an activated hopping over the barrier. The oscillatory long time behavior is damped due to the interaction with the vibration. The deuteron effect is discussed for various temperatures and compares favorably well with experimental data.

*Since September 1968, Dr. Hofacker has been at Technische Hochschule München. The thesis work of R. Rosenstein has been completed under the supervision of S. F. Fischer, Assistant Professor.

PARAMAGNETIC MOLECULAR COMPLEXES

B. M. Hoffman

Assistant Professor, Department of Chemistry

L. Marchant

Ph.D. Thesis Research (NIH Support)

T. Eames

Ph.D. Thesis Research

Objective

This research is aimed at furthering our studies of paramagnetic interactions between a paramagnetic molecule and a complexing diamagnetic molecule, between two paramagnetic molecules, and between pairs of paramagnetic metal ions joined by bridging groups. It is also hoped to gain information about superexchange relevant to a wide class of magnetic insulators from this investigation.

Approach

Complexes of nitroxide free radicals with a variety of group IIIA, IVA and VA halides are being prepared and studied by ESR. Oxo-bridged and chloro-bridged Fe(III) dimers are similarly being prepared and studied, as are monomeric oxygen adducts of cobalt.

Progress

These splittings in conjunction with linewidth and g-factor measurements may be used to define a new acidity scale. Equilibrium measurements provide thermodynamic data in some cases. The ESR of thermally excited quintet states ($S = 2$) has been observed in several oxo-bridged iron dimers. ESR of monomeric cobalt adducts has allowed us to characterize them as superoxide adducts of trivalent cobalt ($\text{Co}^{\text{III}}\text{-O}_2^-$) with the oxygen nuclei unsymmetrically placed with respect to cobalt.

PUBLICATIONS

"EPR of Some Cobalt(II) Schiff Base Compounds and Their Monomeric Oxygen Adducts," B. M. Hoffman, D. Diemente and F. Basolo, J. Am. Chem. Soc., 92, 61 (1970).

"ESR Studies of 1:1 Cobalt-Oxygen Adducts," D. Diemente, B. M. Hoffman and F. Basolo, Chem. Commun., 467 (1970).

INVITED TALKS

"ESR Studies of 1:1 Cobalt-Oxygen Adducts," Ohio State University,
April 1970.

"ESR Studies of 1:1 Cobalt-Oxygen Adducts," Cleveland State University,
April 1970.

PARAMAGNETIC MOLECULAR CRYSTALS

B. M. Hoffman

Assistant Professor, Department of Chemistry

M. Hove

Ph.D. Thesis Research

C. Spilburg

Ph.D. Thesis Research

Objective

The objectives of this research are: (1) to study the magnetic properties of linear chain free radical crystals, relating experiments to theories of spin relaxation in the linear Heisenberg antiferromagnetic chain; (2) to relate the semiconducting properties of these crystals to their magnetic properties; (3) to prepare organic semiconductors doped with donor impurities in a manner similar to the doping of inorganic semiconductors (e.g., as in Si and of eventual use in electronic devices; (4) to examine crystals with paramagnetic metal ions and paramagnetic organic radicals, looking for super- or double-exchange interactions between metal and radical. The overall objective is to prepare and examine new magnetic semiconductors with eventual application in devices which might, for example, be applicable in computer technology, internally couple magnetic and electric circuits without use of inductive coupling or have magneto-optical properties with applications to laser technology.

Approach

Knowledge of the chemistry of these systems permits preparation of crystals possessing properties useful in attaining the objectives stated. The principal investigative tool is electron spin resonance (ESR). However, conductivity studies, optical and infrared spectroscopy and broad line nuclear magnetic resonance are also employed.

Progress

We have performed detailed ESR studies of spin excitations in the ionic charge-transfer complex tetracyanoquinodimethan-tetramethylphenylenediamine (TCNQ-TMPD). The unusual spin-relaxation behavior is interpreted in terms of a theory for the Heisenberg regular linear antiferromagnetic chain. We have observed ESR of delocalized conduction band electrons in a crystal of carbazole doped with TCNQ. Conductivity studies are in progress.

We have determined the crystal structure and performed single crystal ESR studies of the material $[\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2] \cdot [\text{TMPD}]_2$. The magnetic properties are dominated by mobile triplet spin excitons. We have prepared crystals in which paramagnetic Cu(II) replaces diamagnetic Ni(II) and are examining them by x-rays and ESR.

PUBLICATIONS

"ESR of TMPD-TCNQ: Spin Excitations of the Heisenberg Regular Linear Chain," B. M. Hoffman and R. C. Hughes, J. Chem. Phys., 52, 4011 (1970).

ESR AND IR OF ADSORBED FREE RADICALS

B. M. Hoffman

Assistant Professor, Department of Chemistry

G. Lozos

Ph.D. Thesis Research (ARMY Support)

This research is partially supported by the Petroleum Research Fund of the American Chemical Society.

Objective

The objective of this study is to gain information about the bonding of adsorbed species to surfaces of, for example, catalytic interest.

Approach

From ESR parameters of adsorbed free radicals supplemented by IR data, the magnitude of surface interactions can be deduced and inferences made about the nature of surface binding and surface sites.

Progress

We have completed an ESR study of NO adsorbed on surface sites of a silica-alumina catalyst. We have also observed at 77°K the spectrum of nearly freely rotating molecular oxygen trapped at the surface of the catalyst and in the cavities of a molecular sieve. We have initiated ENDOR studies of surface paramagnetic sites.

STRUCTURAL STUDIES BY DIFFRACTION METHODS

J. A. Ibers

Professor, Department of Chemistry

D. Cahen

Ph.D. Thesis Research

B. Frenz

Ph.D. Thesis Research

P. Maltese

M.S. Thesis Research (Completed)

Objective

The general aim of this research project is to learn more about the structure and bonding in the solid state.

Approach

X-ray studies are made of single crystals of closely related chemical substances leading to complete crystal and molecular structure determinations.

Progress

The phase diagrams for the series MF/HF , where M is an alkali metal, are well known, but the types of compounds which exist in these systems are not. Of course, the compound $\text{KF}\cdot\text{HF}$ is known to be $\text{K}^+(\text{FHF}^-)$, and the compound $\text{NaF}\cdot 2\text{HF}$ is known to be $\text{Na}^+(\text{FHFHF}^-)$. We have investigated the nature of the compound $\text{KF}\cdot 4\text{HF}$ and find it to be $\text{K}^+(\text{H}_4\text{F}_5^-)$. The H_4F_5^- ion consists of a central F atom approximately tetrahedrally surrounded by four other F atoms. The central F atom is connected to the peripheral F atoms through unsymmetric F-H-F bonds.

The structure of the compound $\text{CoH}(\text{PF}_3)_4$ has been investigated at -120° . In recent years the PF_3 ligand has been shown to resemble closely the CO ligand and to lead to increased stability of the analogous complexes. Thus $\text{CoH}(\text{PF}_3)_4$ is the direct analogue of $\text{CoH}(\text{CO})_4$, the classic transition metal carbonyl hydride. The structure of the latter compound remains undetermined by diffraction methods because of its instability. The present structure determination has revealed an approximate tetrahedral arrangement of PF_3 groups about the center Co. Of significance to inorganic chemists is the very short Co-P distance of 2.05 Å, some 0.2 Å shorter than Co- PR_3 distances, where R is alkyl or aryl. Thus this study provides direct evidence for multiple bonding in metal $-\text{PF}_3$ complexes.

PUBLICATIONS

- "An X-ray Study of α -Oxalic Acid Dihydrate, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, and of its Deuterium Analogue, $(\text{COOD})_2 \cdot 2\text{D}_2\text{O}$: Isotope Effect in Hydrogen Bonding and Anisotropic Extinction Effects," R. G. Delaplane and J. A. Ibers, *Acta Cryst.*, **B25**, 2423 (1969).
- "An Experimental Determination of the Asphericity of the Atomic Charge Distribution in Oxalic Acid Dihydrate," P. Coppens, T. M. Sabine, R. G. Delaplane and J. A. Ibers, *Acta Cryst.*, **B25**, 2451 (1969).
- "The Structure of Potassium Tetrahydrogen Pentafluoride," B. A. Coyle, L. W. Schroeder and J. A. Ibers, *J. Solid State Chem.*, **1**, 386 (1970).

INVITED TALKS

"Bonding of Small Molecules to Transition Metals"

Illinois Institute of Technology, October 1969
American Chemical Society, Local Sections at Richland and Pullman, Washington, March 1970
University of Missouri, April 1970
Seton Hall University, April 1970
Carnegie-Mellon Institute, May 1970

"Some Topics in Hydrogen Bonding"

University of Virginia, April 1970

"Current Status of Structural Crystallography"

American Chemical Society, Local Sections at Spokane and Seattle, Washington, March 1970

STRUCTURES AND PROPERTIES OF TRANSITION METAL COMPLEXES

J. A. Ibers
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Postdoctoral Research Associate

This research is supported primarily by the National Science Foundation.

Objective

This research is aimed at characterizing accurately the structures of interesting transition metal complexes, with special emphasis on the intercomparisons of closely related complexes.

Approach

X-ray studies are made of single crystals leading to complete crystal and molecular structure determinations.

Progress

Our studies of metal-silicon bonds have continued. We have now provided definitive evidence, through a series of diffraction studies, that transition metal-silicon bonds are shorter than one would predict in the absence of some multiple bonding. This is of importance in understanding the differences between metal-carbon and metal-silicon chemistry.

Our studies of five-coordinate transition metal complexes have continued. In particular, we have completed several MX_5 complexes and the trends between axial and equatorial bond lengths in trigonal bipyramids are in accordance with predictions made on the basis of our previous work on the $CuCl_5^{3-}$ system.

PUBLICATIONS

"A Simple Cold Gas Flow Apparatus," B. A. Frenz, J. H. Enemark, L. W. Schroeder, D. J. Hodgson, W. T. Robinson, R. J. Loyd and J. A. Ibers, J. Appl. Cryst., 2, 112 (1969).

- "Nature of the Donor-Acceptor Bond in Acetonitrile-Boron Trihalides. The Structures of the Boron Trifluoride and Boron Trichloride Complexes of Acetonitrile," B. Swanson, D. F. Shriver and J. A. Ibers, *Inorg. Chem.*, 8, 2182 (1969).
- "The Structure of Chlorodicarbonyl-bis(triphenylphosphine) iridium(I)-benzene," N. C. Payne and J. A. Ibers, *Inorg. Chem.*, 8, 2714 (1969).
- "Geometries of Transition Metal Complexes Containing Simple Alkenes," L. Manojlovic-Muir, K. W. Muir and J. A. Ibers, *Discussions Faraday Soc.*, 47, 84 (1969).
- "The Crystal Structure of Solvated Hydridochloro(trichlorosilyl) bis(triphenylphosphine)rhodium, $\text{RhHCl}(\text{SiCl}_3)(\text{P}(\text{C}_6\text{H}_5)_3)_2 \cdot \text{SiHCl}_3$," K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 9, 440 (1970).
- "The Crystal and Molecular Structure of Hydridobis(trichlorosilyl) carbonyl-pi-cyclopentadienyl-iron, $(\text{pi-C}_5\text{H}_5)\text{FeH}(\text{SiCl}_3)_2(\text{CO})$," L. Manojlovic-Muir, K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 9, 447 (1970).
- "Five-Coordinate Nickel(III). The Crystal and Molecular Structure of $\text{NiBr}_3(\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2)_2 \cdot 0.5\text{NiBr}_3(\text{P}(\text{C}_6\text{H}_5)(\text{CH}_3)_2) \cdot \text{C}_6\text{H}_6$," J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 9, 453 (1970).
- "The Crystal Structure of Hexaamminecobalt(III) tetrachlorozincate (II) Chloride, $(\text{Co}(\text{NH}_3)_6)(\text{ZnCl}_4)\text{Cl}$," D. W. Meek and J. A. Ibers, *Inorg. Chem.*, 9, 465 (1970).
- "The Structure of Pentakis(2-picoline-N-oxide)cobalt(II) Perchlorate, $(\text{Co}(\text{C}_5\text{H}_7\text{NO})_5)(\text{ClO}_4)_2$," B. A. Coyle and J. A. Ibers, *Inorg. Chem.*, 9, 767 (1970).
- "A Cobalt-Germanium Bond: The Structure of $\text{Co}(\text{Ge}(\text{C}_6\text{H}_5)_3)(\text{CO})_3(\text{P}(\text{C}_6\text{H}_5)_3)_2$," J. K. Stalick and J. A. Ibers, *J. Organometal. Chem.*, 22, 213 (1970).
- "The Crystal and Molecular Structure of Dinitrosylbis(Triphenyl-phosphine) Iridium Perchlorate, $(\text{Ir}(\text{NO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2)(\text{ClO}_4)$," D. Mingos and J. A. Ibers, *Inorg. Chem.*, 9, 1105 (1970).
- "Preparation and Structure of a Novel Tetracyanoethylene Complex of Iridium," J. S. Ricci, J. A. Ibers, M. S. Fraser and W. H. Baddley, *J. Amer. Chem. Soc.*, 92, 3489 (1970).

INVITED TALKS

"Transition Metal Hydrides"

University of Oregon, March 1970

Montana Section, American Chemical Society, March 1970

STRUCTURES OF SYNTHETIC MOLECULAR OXYGEN CARRIERS AND RELATED COMPLEXES

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C. Pratt
Ph.D. Thesis Research

H. Stynes
Ph.D. Thesis Research

This work is supported primarily by the National Institutes of Health.

Objective

The main objective of this work is to prepare and determine the molecular structures of synthetic molecular oxygen carriers and related complexes and thereby deduce possible factors contributing toward the bonding of molecular oxygen to transition metals.

Approach

Synthesis of various complexes are undertaken, followed by x-ray studies of single crystals leading to complete structure determinations.

Progress

Work has continued on transition metal-olefin complexes and transition metal nitrosyl complexes. Significant progress has been made on defining the geometries of some simple olefins, such as tetracyanoethylene, when bound to the same transition metal systems which also take up molecular oxygen. Similarly, we now have a much firmer understanding of when the nitrosyl ligand, NO, will bond to transition metals as NO⁺ (isoelectronic with CO) and when it will bond as NO⁻ (isoelectronic with O₂).

PUBLICATIONS

"The Role of the Metal Atom in the Reversible Uptake of Molecular Oxygen. The Structures of the Molecular Oxygen Complexes Formed by Bis(bis(diphenylphosphine(ethane)iridium(I) Hexafluorophosphate and its Rhodium Analog," J. A. McGinnety, N. C. Payne and J. A. Ibers, J. Am. Chem. Soc., 91, 6301 (1969).

- "The Bonding of Molecular Nitrogen. I. The Crystal and Molecular Structure of Hydridodinitrogentris(triphenylphosphine)cobalt(I)," B. R. Davis, N. C. Payne and J. A. Ibers, *Inorg. Chem.*, 8, 2719 (1969).
- "The Structure and Absolute Configuration of (+)₄₅₀-cis-dichlorobis(ethylenediamine)platinum(IV) Chloride, $(\text{Pt}(\text{C}_2\text{H}_4\text{N}_2)_2\text{Cl}_2)\text{Cl}_2$," G. F. Liu and J. A. Ibers, *Inorg. Chem.*, 9, 773 (1970).
- "The Structure of Bis(t-butylnitrosyl)(tetracyanoethylene)nickel(0), $\text{Ni}((\text{CN})_2\text{C}=\text{C}(\text{CN})_2)((\text{CH}_3)_3\text{C}-\text{N}=\text{O})_2$," J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, 92, 5333 (1970).

INVITED TALKS

"Oxidative Addition Reactions and Structures"

Massachusetts Institute of Technology, November 1969
University of Illinois, Urbana, November 1969

"Model Systems for Oxygen and Nitrogen Bonding"

Gordon Research Conference on Metals and Metal Binding in Biology,
August 1970.

SINTERING OF METALS AND CERAMICS

D. L. Johnson

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A. Doi

Ph.D. Thesis Research

Objective

The model which has been developed is being employed to investigate the sintering of compacts of spherical particles of LiF with and without addition of MgF_2 . The principal objective is to study the mechanisms of material transport in the isothermal and non-isothermal sintering, and how these mechanisms are influenced by minor additives and atmospheric environment. Lithium fluoride was chosen as a material for study because it is a well characterized ionic solid in which both cation and anion volume diffusion coefficients are known. The solubility of MgF_2 in LiF and its effect on ionic conductivity have also been investigated.

Although it is known that small amounts of additives often have a large effect on sintering of both ceramics and metals, there has been no work reported in which the effects have been satisfactorily explained--the definitive experiments just haven't been done. With our experimental techniques, it is now possible to clearly determine the sintering mechanism and the effects of impurities and atmospheric environment on these mechanisms, even though two or three are acting in concert. Such an understanding will assist the optimization of the sintering of materials.

Approach

The sintering shrinkage of compacts of closely sized spherical particles is followed continuously with a recording dilatometer. At the end of the run, which results in 5% or less linear shrinkage, the compacts are sectioned and the average neck size between spheres is measured metallographically. With this information, the model can be utilized to compute the volume, grain boundary, and surface diffusion coefficients, and the contributions of each of these to the sintering process.

Non-isothermal sintering studies are conducted on the same types of compacts under conditions of approximately linear heating and also cyclic heating and cooling. The latter provides a quick and easy test for the existence of significant surface diffusion, and it yields the true activation energy of the densification mechanism.

Known amounts of MgF_2 are added in solid solution, and the effect thereof on sintering is determined. A simplified model predicts that MgF_2 should increase volume diffusion of Li and decrease that of F, through the introduction of lithium vacancies. Thus the rate-controlling species can be determined with greater confidence.

In order to confirm the indications that fluorine is considerably enhanced in the grain boundaries, the ionic conductivity of single and polycrystalline LiF will be investigated.

Progress

The transient enhanced densification of compacts of spherical particles of "pure" LiF is probably caused either by dislocation motion or by recovery processes as the spherical particles are heated. After this transient has subsided the sintering proceeds as predicted for the rate being limited by volume diffusion of lithium. This implies that fluorine is enhanced in the grain boundaries, while lithium is not. Such effects have been found by others for tracer self diffusion in K and Na halides.

Vapor transport, surface diffusion and grain boundary diffusion are not significant near the melting point of LiF for the 50 μm diameter particles studied.

Methods of obtaining uniformly-doped powders are currently under investigation.

Further examination of Seidel's data (M.S. Thesis, Northwestern University (1969), 1969 Annual ARPA Technical Report, p. 95) indicates that the grain boundary self-diffusion coefficient is increased about 4 times in air compared with purified argon at 900°C, while the volume coefficient is unchanged.

PUBLICATIONS

"Effect of TiO_2 on Initial Sintering of Al_2O_3 ," R. D. Bagley, I. B. Cutler and D. L. Johnson, J. Amer. Ceram. Soc., 53, 136 (1970).

THEORY OF SINTERING

D. L. Johnson

Associate Professor, Department of Materials Science

The isothermal initial stage sintering studies were supported by ARPA, the non-isothermal and intermediate stage studies were supported by ARO-D.

Objective

For many years various investigators have attempted to describe the sintering process in terms of its most fundamental parameters. A common failure of all previous attempts has been the inability to obtain quantitative results if more than one mechanism of material transport is operative. The primary goal of this project is to develop models for use in analyzing the sintering behavior of materials. In particular, it is desirable to determine the material transport mechanisms that are significant, and the appropriate transport parameters (i.e., diffusion coefficients). Also of importance is the prediction of sintering behavior, given the transport parameters, the temperature as a function of sintering time, the surface tension, the average particle shape, size and size distribution.

Successful models will make it possible not only to determine the significant material transport phenomena, but also to study the effects of additives and atmosphere on these phenomena and therefore on the sintering behavior. Such an understanding will contribute to optimization of the sintering process.

Approach

The initial-stage sintering models are obtained by writing the mass flux equations for each transport process (i.e., volume diffusion, grain boundary diffusion, surface diffusion, and vapor transport) in terms of the instantaneous geometry of the particles that are undergoing sintering. The computer is employed to synthesize the sintering behavior on the basis of these flux equations and the other necessary parameters. The temperature can be programmed as a function of time so that non-isothermal, as well as isothermal, sintering curves can be constructed. The basic flux equations can be used for a wide range of particle geometries, making it possible to investigate the effect of particle shape on expected sintering behavior.

The significant factors during the intermediate stage of sintering are being considered in order to determine a general model for that stage of sintering.

Progress

Gessinger [Scripta Met. 4, 674 (1970)] suggested that, under conditions where surface and volume diffusion are both much less significant than grain

boundary diffusion, the densification would be controlled by volume diffusion. This is because the material which arrives at the neck surface via grain boundary diffusion must be redistributed over the neck surface. He failed to realize that at low temperatures surface diffusion could be rate controlling. Calculations indicate surface diffusion may be rate controlling in silver at lower temperatures and shrinkages.

PUBLICATIONS

"Discussion of 'Volume Diffusion as Densification Rate-controlling Step in Sintering'," Scripta Met., 4, 677 (1970).

"The Use of Phase Diagrams in the Sintering of Ceramics and Metals," I. B. Cutler and D. L. Johnson, Phase Diagrams, Vol. 2, Ed. by A. M. Alper, Academic Press, New York (1970).

"A General Model for the Intermediate Stage of Sintering," D. L. Johnson, J. Amer. Ceram. Soc., 53, 574 (1970).

INVITED TALKS

"Sintering of Metals and Ceramics," University of Illinois, Urbana, March 1970.

"Methods of Determining Sintering Mechanisms," International Powder Metallurgy Conference, New York, July 1970.

"Capillarity Phenomena in Solids," Summer Session Course at Department of Ceramic Engineering, University of Washington, July and August 1970.

SINTERING MECHANISMS OF CoO

D. L. Johnson

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P. Kumar

Ph.D. Thesis Research

S. O. Brennom

M.S. Thesis Research

This research is supported by the U. S. Army Research Office-Durham.

Objective

The objective of this research is to study the sintering mechanisms of a nonstoichiometric oxide. Cobalt oxide has been selected because the cation and anion volume self-diffusion coefficients and the surface diffusion coefficient have been measured by tracer techniques and the composition as a function of the partial pressure of oxygen and temperature has been determined. The mechanisms of sintering and the kinetics and energetics of the process are being investigated as functions of temperature and composition. The initial-stage sintering of compacts of spherical and non-spherical particles, as well as intermediate-stage sintering, is being investigated.

Approach

Spherical particles of CoO have been obtained by dropping the powder through an oxygen-gas heated magnesia tube. These spheres are sized to obtain narrow size-range fractions. Compacts are prepared without pressing and sintered isothermally in a controlled P_{O_2} atmosphere using mixtures of carbon monoxide and carbon dioxide or argon and oxygen. Compact shrinkage is measured continuously on a strip chart recorder and the compacts are sectioned and the neck size is measured at the end of the run. The measurement of the shrinkage and the neck size and the shrinkage rate allows the determination of the volume and grain boundary contributions to sintering, as well as the surface diffusion contribution. The intermediate-stage measurements are made on as-received powder which has been compacted and sintered isothermally. A series of compacts are sintered at one temperature for varying amounts of time. The densification rate at the end of each run is determined from the strip chart record. The compacts are then impregnated and sectioned and the necessary geometric parameters are determined by quantitative metallography techniques. As a result of the measurements, not only are the densification kinetics determined but the occurrence of grain growth and pore growth are also determined quantitatively. Thus, a rather complete picture of the sintering process is obtained.

Progress

The sintering of spherical particles has been carried out at 1100°, 1200°, and 1300°C and at P_{O_2} of 10^{-3} and 0.8 torr. The rate is greater for higher P_{O_2} , which is an indication that volume diffusion of cobalt is rate controlling. The spheres undergo marked faceting, so that the initial stage model cannot be applied. The faceting leads to polyhedral pores during the later stages of sintering. Since plane surfaces present no driving force for sintering, there is substantial retained porosity. The intermediate stage sintering rate is consistent with a rate controlled by volume diffusion of Co, even though the reported Co diffusion coefficient is $\sim 10^5$ greater than that for oxygen. This implies a very rapid grain boundary diffusion of oxygen so that the metal to oxygen ratio is preserved.

AMORPHOUS SEMICONDUCTORS

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Objective

Recently a number of amorphous semiconductors have been reported in the literature which exhibit various types of switching behavior. Attention to such effects in non-crystalline semiconductors has resulted chiefly from the wide spread publicity given to the so-called ovonic device introduced by the Energy Conversion Devices Company. Although many compositions currently being discussed in regard to switching behavior are new in the semiconductor literature, other properties were examined earlier from the standpoint of potential useful glass forming compositions. The present work was undertaken to confirm some of the observations reported for amorphous semiconductors and to observe switching effects in selected compositions which had not been previously investigated.

Approach

A systematic examination of glass forming compositions was made which included compositions containing three, four, five and higher numbers of chemical elements as principal constituents. A correlation was made between the most favorable semiconductor-switching behavior previously reported and the composition charts. Based on these observations, ingots of six different compositions were synthesized in amorphous form. Samples were then prepared for observing switching effects. Both electrical and optical gating were tried with the results observed on oscillograph patterns.

Progress

Although various compositions have been reported as exhibiting ovonic behavior, some were found to show no switching, or rather marginal effects; others did show switching as predicted. In previous work compositions containing antimony had not shown switching behavior although the majority of successful compositions contained arsenic.

It was found that very few glass forming compositions contained antimony that also contained one or more of the elements arsenic, tellurium and thallium which appear to be key elements in promoting the switching effects in amorphous materials. Compositions $\text{Si}_{10}\text{As}_8\text{Sb}_2\text{Te}_{20}$ and $\text{As}_{14}\text{Tl}_{14}\text{Sb}_8\text{Se}_{18}\text{Te}_{21}$ were prepared. The first showed no transition to a low resistance state. The second composition showed switching behavior on a sine wave from frequencies of 20 Hz to 500 kHz. Many aspects of the change between the high and low sensitivity states were investigated including laser control of the resistivity change. Other compositions, not containing antimony, were also prepared which exhibited switching effects.

ELECTRONIC PROPERTIES OF GERMANIUM ARSENIDE SEMICONDUCTORS

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M.S. Thesis Research (Bell Telephone Laboratories Cooperative Student)

Objective

The program of work on the germanium arsenide semiconductors is continuing. In view of the result of the initial optical and electrical measurements the next phase will be to extend optical measurements and to develop samples with higher carrier mobilities.

Approach

To improve sample composition other methods will be employed to prepare samples that have mobilities greater than $100 \text{ cm}^2/\text{V-sec}$. In view of the initial analysis of optical measurements, information concerning intrinsic activation energies and higher band transitions is incomplete. Reflectivity measurements will now extend the phonon energy range to 12 eV. From these and previous results a tentative energy band scheme will be proposed for a limited range of the Brillouin zone.

Progress

The second phase of the GeAs-GeAs₂ investigation has just been recently initiated. Preliminary calculations are in progress on simple band structure configurations. Instrumentation problems are concerned with sample preparation-sample chamber construction for the vacuum ultraviolet spectrophotometer.

PUBLICATIONS

"Transmission and Reflection Measurements on Small Crystalline Samples Using the MM12 Monochromator," J. W. Rau and C. R. Kannewurf, Zeiss-Mitteilungen, 5, No. 4, 199 (1970).

"Optical and Electrical Properties of the Semiconductors GeAs and GeAs₂," J. W. Rau and C. R. Kannewurf, Bull. Am. Phys. Soc., 15, 31 (1970).

"Optical Properties of Single Crystal Silicon Arsenide," L. C. E. Miller and C. R. Kannewurf, J. Phys. Chem. Solids, 30, 849 (1970).

"A Pulsed GeAs Laser System for Semiconductor Carrier Lifetime Measurements," M. E. Motamedi and C. R. Kannewurf, IEEE Transactions on Instrumentation and Measurement IM-19, 6 (1970).

"Electrical and Optical Properties of the Semiconductors TiS , $\text{TiS}_{0.5}\text{Se}_{0.5}$ and TiSe ," R. S. Itoga and C. R. Kannewurf, Bull. Am. Phys. Soc., 15, 285 (1970).

NARROW BAND GAP SEMICONDUCTORS

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Associate Professor, Department of Electrical Engineering

C. A. Gao
M.S. Thesis Research

Objective

To investigate a narrow band gap semiconductor-semimetal for possible use as an extrinsic photodetector or for a possible superconducting transition. Several binary systems will be examined to see if either effect is present.

Approach

The initial samples will be synthesized to ascertain whether single crystal material can be prepared by conventional methods. Preliminary measurements will include resistivity data from 1°K to the sample melting point and estimates of principal activation energies.

Progress

This program has just been initiated. Equipment for sample preparation is being assembled and some preliminary work in progress.

PHYSICAL AND ELECTRONIC PROPERTIES OF ORGANIC SEMICONDUCTORS

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J. W. Kauffman
Professor, Department of Materials Science

D. A. Miller
Ph.D. Thesis Research (Completed)

R. A. Arndt
Brookhaven National Laboratory

Objective

To investigate selected physical properties of phenanthrene, in order to better interpret phenomena observed in the fused-ring aromatic hydro-carbons. The emphasis in this investigation has been a detailed study of dielectric and dilatation phenomena in phenanthrene.

Approach

Although anthracene and phenanthrene are structural isomers, several anomalous phenomena have been observed in phenanthrene that have not been found in the more widely studied anthracene. To further explain these effects, dielectric permittivity and dilatation measurements were performed over the temperature interval where the anomalies occur. A major effort in this work has been instrumentation for such measurements on small organic crystals.

Progress

High-purity, single crystal specimens have been provided through the courtesy of researchers at Brookhaven National Laboratory. Capacitance data on single crystal phenanthrene have been obtained from 25 to 75°C using a capacitance bridge capable of resolving changes on the order of 10^{-8} pF. The measured capacitance has been found to depend upon frequency, temperature, rates of temperature change, and on the thermal history of the specimen. A specially designed capacitance-type dilatometer has been employed to observe length changes on the order of 100 Å in 5mm specimens over the temperature range of 24 to 82°C. In the vicinity of 73°C, the thermal expansion coefficient peaks sharply along the direction of the a and c' axes of the monoclinic structure and dips sharply along the direction of the b axis, the two-fold symmetry axis. A molecular model is proposed which is consistent with the observed dielectric and dilatometry measurements

and also with other anomalous properties previously reported in the literature which includes heat capacity, resistivity and electrical polarization phenomena.

PUBLICATION

"Dilatation Studies on Single Crystal Phenanthrene," D. A. Miller, J. W. Kauffman, R. A. Arndt, and C. R. Kennecurf, Bull. Am. Phys. Soc., 15, 286 (1970).

SUPERCONDUCTIVITY IN THE γ -PHASE OF THE Tl-Te SYSTEM

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A. G. Juodakis

Ph.D. Thesis Research

This research is supported by the National Science Foundation.

Objective

To investigate various aspects of the occurrence of a superconducting state and related phenomena in the γ -phase of the Tl-Te system.

Approach

Many samples with varying composition and impurity concentration are prepared for investigating the transition to the superconducting state as a function of composition, carrier concentration, crystal structure change, etc. throughout the range of γ -phase composition. In addition to galvanomagnetic studies, heat capacity and other measurements are in progress.

Progress

Heat capacity studies have been undertaken as a joint program with researchers at Bell Telephone Laboratories, Murray Hill. Initial results indicate the existence of a superconducting state in the heat capacity data at the same temperature found in the magnetic measurements, but the interpretation of the data is far from complete as the behavior is not typical of other superconductors.

A zone melting method has now been further improved for γ -phase material at the stoichiometric composition. Techniques have also been developed for preparing samples of this very brittle material, a fraction of a millimeter thick, with surface areas over 150 square millimeters for improved galvanomagnetic measurements; electrode-contact problems have been minimized with special soldering procedures. It is felt that poor methods employed in these operations are chiefly responsible for the wide variation in electrical data reported in the literature.

ELECTRICAL PROPERTIES OF LIQUID CRYSTALS

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D. G. Shaw

Ph.D. Thesis Research

Objective

The electrical and the corresponding structural properties of the organic compounds exhibiting a "liquid crystalline" mesomorphic state are being studied in an effort to learn about the electrical nature of these mesomorphic states and their phase transitions.

Approach

The "liquid crystal" structural changes observed in the solid-mesomorphic, mesomorphic-mesomorphic, and mesomorphic-isotropic liquid transitions are reflected in abrupt changes in resistivity, dielectric loss, Hall voltage, and power factor, as well as x-ray diffraction structural factors. The study of these electrical and structural properties will enable us to characterize these mesomorphic transitions.

Progress

Resistivity and dielectric resonance bridge-type measuring apparatus has been set up that will enable us to make dielectric measurements with a high degree of accuracy. Also, magnetic facilities have been temporarily obtained and installed to determine magnetic field effects on these measurements. The conductivity of the cholesteric liquid crystals has been determined both as a function of applied voltage and temperature. The functional relationship between the real and imaginary dielectric constant and temperature and electric field frequency has been determined. A characterization of the electrical properties of cholesteric liquid crystals is almost completed.

We plan to extend these dielectric measurements to include the smectic and nematic liquid crystals to permit complete dielectric characterization of the liquid crystal state. We plan to investigate the biological significance of the electrical measurements since these liquid crystalline structures are found in most biological membranes.

DIFFRACTION STUDIES OF SELENIDE-HALIDE COMPLEXES

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D. H. Johnson
Ph.D. Thesis Research (NIH Fellow)

This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

The complexes of molecular halogens (Cl_2 , Br_2 , I_2) with organic sulfides (R_2S), selenides (R_2Se), and tellurides (R_2Te) can exist in several structural forms: polar ($\text{R}_2\text{S}^+-\text{Br}^-$), covalent (R_2SeBr_2), molecular complex ($\text{R}_2\text{Se}\cdots\text{Br}_2$). It is our objective to clarify the nature of the bonding in these complexes in both the solid and the liquid states.

Approach

The molecular structure of a selected complex (selenane dibromide) is being determined by X-ray crystallography. NMR, IR, Raman, and UV spectra and conductance data are also being obtained for an entire series.

Progress

Sufficient X-ray data on the selenium dibromide have been obtained to warrant the conclusion that the geometry around selenium is a trigonal bipyramid, with covalently bound bromines at the axial positions. This structure can be altered, however, if either the halogen or the Group-VI atom is changed. We have found that the sulfur dibromide is primarily ionic in solution and a molecular complex in the solid. Interestingly, crystals of the sulfur diiodide are strongly thermochromic. They vary from maroon at 25°C to light yellow at -180°C . The color becomes lighter as the $\text{S}\cdots\text{I}\cdots\text{I}$ complex is transformed to a $\text{S}-\text{I}\cdots\text{I}$ species. These complexes provide a wide variety of structural types and will continue to warrant investigation.

PREPARATION OF NOVEL METAL-ORGANIC COMPLEXES

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D. E. Stedman
Ph.D. Thesis Research

R. R. Clikeman
Ph.D. Thesis Research

Objective

New bonding situations are being developed between metal atoms and organic ligands. The structural and chemical properties of these novel complexes will be investigated.

Approach

We are preparing complexes between cyclopropanes and transition metals. The olefin-metal complexes have been thoroughly studied, and these successes led us to believe that the electronically similar cyclopropane ring would enter into complex formation. Structure-bonding questions are being answered by appropriate spectroscopic and diffraction experiments. We are also preparing complexes between transition metals and fluorocarbon ligands. The presence of the fluorine atoms should enhance the stability of these complexes.

Progress

We have succeeded in preparing several platinum-cyclopropane complexes. We are interested in obtaining both static and dynamic information about their structures. It appears that the parent complex is best represented as a cyclobutane-like structure, in which there is a trimethylene-platinum four-membered ring. The ^1H spectrum and in particular the ^{195}Pt sidebands of the ligand resonance are in accord with a non-fluxional structure. We plan to examine the ^{13}C NMR spectrum of this complex as well. Substituted cyclopropane-platinum complexes have also been prepared, but as yet all attempts to produce palladium analogues have failed. We have just begun the synthesis of the fluorocarbon ligand $-\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2-$, which should be able to form stable cyclic complexes with transition metals.

MAGNETIC RESONANCE AND VIBRATIONAL SPECTROSCOPIC STUDIES

- J. B. Lambert
Associate Professor, Department of Chemistry
- D. S. Bailey
Postdoctoral Research Associate (Sloan Supported) (Completed)
- W. L. Oliver, Jr.
Ph.D. Thesis Research (NIH Fellow) (Completed)
- J. L. Cosnell
Ph.D. Thesis Research (NDEA Fellow) (Completed)
- C. E. Mixan
Ph.D. Thesis Research
- L. G. Greifenstein
Ph.D. Thesis Research

This research is primarily supported by the National Science Foundation.

Objective

By suitable spectroscopic experiments (NMR, IR, Raman), we plan to elucidate the structure and conformation of flexible molecules.

Approach

Structural information is extracted from NMR spectra by analysis for the coupling constants (J). Specific information about the steric arrangements of atoms is obtained in this fashion. Comparison of infrared and Raman spectra gives further structural information.

Progress

We have completed our structural study of cyclopropene and presented a general review of the field of conformational analysis. We have continued our work with the R value, by which structural parameters may be obtained for molecules in solution. We have also studied the effects of structure on inversion about nitrogen. Some spectral studies of cyclic organophosphines have been completed. These investigations involved NMR as the prime structural tool. We have also utilized IR and Raman spectroscopy for the determination of the symmetry properties of various organic compounds, in particular N-nitroso- and N-nitroamines.

PUBLICATIONS

"The Shapes of Organic Molecules," J. B. Lambert, Scientific American, 222, 58 (1970).

"Analysis of the Proton Magnetic Resonance Spectrum of Cyclopropene," J. B. Lambert, A. P. Jovanovich, and W. L. Oliver, Jr., J. Phys. Chem., 74, 2221 (1970).

INVITED TALKS

"Homoconjugation"

Case-Western Reserve University, Cleveland, Ohio, January 1970.

University of Cincinnati, April 1970.

"Nuclear Magnetic Resonance Spectroscopy"

ACS Short Course, Anaheim, California, October 1969.

Wheaton College, October 1969.

ACS Short Course, Houston, Texas, February 1970.

ACS Short Course, New York, New York, May 1970.

SURFACE REACTIONS ON ALKALI HALIDES

J. E. Lester

Assistant Professor, Department of Chemistry

W. F. Marx

Ph.D. Thesis Research

N. J. Sell

Ph.D. Thesis Research

Objective

To study the interactions and reactions of impinging molecules with an alkali halide crystal surface. These studies should yield information on the energetics of molecules adsorbed on these surfaces and on the mechanisms of vaporization of alkali halide crystals.

Approach

A thermal molecular beam of ionic molecules MX is impinged on a crystal surface (NY) and the scattered MX and reaction products are measured. The angular distributions of products, product ratios, temperature dependence of products, and residence times of products on the surface are measured by a mass spectrometer. From these data activation energies for the several processes taking place may be calculated.

Progress

Two systems have been studied: (a) NaBr(v) impinging on KCl(s) and (b) KBr(v) on NaCl(s). The product ions observed with the mass spectrometer in (a) are NaBr^+ , NaCl^+ , Na_2Cl^+ , NaKCl^+ , KBr^+ , KCl^+ and K_2Cl^+ . The last two are present in the absence of an impinging beam at the crystal temperatures used since they are vaporization species of KCl. The first is due to reflected beam molecules. Decay times for NaBr^+ , NaCl^+ , NaKCl^+ and KBr^+ have been measured on a time scale of seconds. At a surface temperature of 450°C the NaCl^+ and NaKCl^+ decay times on shuttering the NaBr beam are on the order of 90 and 40 sec, respectively. The other decay times are as fast as the instrumental response. These results probably demonstrate the importance of diffusional processes in the formation of the molecular precursors of these ions. Similar results have been found for KBr(v) on NaCl(s). Here KCl^+ and NaKCl^+ have appreciable decay times. The product ion intensities are far from what would be predicted from equilibrium thermodynamic considerations. Temperature dependences of the product intensities are being measured.

VAPORIZATION KINETICS OF IONIC CRYSTALS

J. E. Lester

Assistant Professor, Department of Chemistry

W. P. Dianis

Ph.D. Thesis Research

C. A. Pierce

Undergraduate Honors Research

This research is supported by the National Science Foundation.

Objective

To study the effect of impurities and other crystal defects on the vaporization kinetics of simple ionic solids. To investigate the mechanisms involved in the vaporization process for these simple solids.

Approach

Vaporization rate measurements are made for one face of a single crystal of the solid under study. The single crystals are as well characterized as possible. Typical dislocation densities and impurity concentrations at the ppm level are determined for adjacent sections of the original boule. The influence of changes of a defect concentration in the crystal on the vaporization rate of the (100) face is determined for defects such as dislocations and specific impurities. We will attempt to correlate these variations in the vaporization rate to solid-state properties of the crystal in an attempt to derive a reliable mechanism of vaporization for this type of solid.

Progress

A combined zone refining and Kyropoulos crystal growth apparatus similar to one designed by Pohl and co-workers is being built in order to reduce undersized impurities in the crystals to a few ppm. Zone leveling may be employed to introduce impurities prior to crystal growth. Using a specially purified hydrogen halide gas ambient atmosphere during zone refining considerably reduces the OH^- concentration in the crystal.

Single crystal CsCl crystals have been grown from solution. The crystals contain about .01% NH_4^+ from the growth solution. A phase transformation from the CsCl to the NaCl lattice at 469°C and the cation, the more slowly diffusing ion in this lattice, makes this solid very interesting. We have observed that the vaporization rate rises discontinuously when the crystal transforms to the high temperature phase. It is necessary to raise the crystal several degrees above the transition temperature in order to effect the phase transition in a short time. Going through the transition temperature from above produces a discontinuous drop

in the rate. We are presently growing Ba^{++} doped CsCl crystals to determine the effect of a divalent impurity on the vaporization rate of this solid and on the phase transition.

PUBLICATIONS

"Off-Axis Channeltron Multiplier for Quadrupole Mass Spectrometers,"
J. E. Lester, Rev. Sci. Instr., 41, 1513 (1970).

PROPERTIES OF ZERO-GAP SEMICONDUCTOR

L. Liu

Associate Professor, Department of Physics

Objective

The objective of this research is a theoretical study of the unusual dielectric screening and other related electronic properties of semiconductors with zero-gap in their single-particle energy spectrum.

Approach

We continue to use the same general approach as previously reported. This includes evaluation of wave functions near the degenerate band edge by $\vec{k} \cdot \vec{p}$ perturbation theory and calculation of the static dielectric function under the random-phase-approximation. However, important improvements have been made concerning the calculation of impurity-limited mobility in a degenerate n-type sample of zero-gap semiconductors. We now use Bloch-waves instead of plane-waves in evaluating both the intra-band electronic polarizability and the intra-band scattering matrix element.

Progress

We have shown that the Bloch wave character of degenerate donor electrons in a zero-gap semiconductor like α -Sn causes significant reduction in the intra-band polarizability $\chi(q)$ from the corresponding free-electron values over the entire range of q -values of interest (from $q=0$ to $q=2k_f$, where k_f is the Fermi momentum). This factor, in turn, causes a reduction in the impurity-limited mobility. However, if Bloch waves are also used in the intra-band impurity scattering, the calculated mobility with enhanced inter-band polarizability previously obtained and the reduced intra-band polarizability is still too high as compared with the experimental values. The reason for this discrepancy is currently being investigated.

PUBLICATION

"Dielectric Enhancement and Mobility of α -Sn," Phys. Rev., B15, (1970).

INVITED TALK

"Dielectric Constant and Enhanced Mobility in Zero-Gap Semiconductors," Solid State Seminar, Physics Department, Purdue University, February 1970.

ANOMALOUS LONGITUDINAL MAGNETORESISTANCE

J. A. Marcus
Professor, Department of Physics

W. A. Reed
Bell Telephone Laboratories

This research is jointly supported by the Advanced Research Projects Agency, the National Science Foundation and Bell Telephone Laboratories.

Objective

The objective of this research is to determine if the "zero resistance" in a longitudinal magnetic field observed in several metals can be explained with a theoretical model based on an anisotropic current distribution resulting from poor lead geometry and a highly anisotropic magnetoconductivity.

Approach

The approach is to solve the classical problem of the current distribution in a metal in which the resistance parallel to the current direction is very much less than in a direction perpendicular to the current flow and check the theory by measurements on a metal for which the phenomenon had not previously been observed.

Progress

The calculations fully accounted for the observations in chromium and were further verified by measurements on high purity single crystals of tungsten.

PUBLICATIONS

"Comments on Zero Resistance in a Longitudinal Magnetic Field——," J. A. Marcus and W. A. Reed, *Phys. Rev. Letters*, 24, 503 (1970).

INVITED TALKS

"Negative Magnetoresistance in Metals," University of Toronto, Toronto, Ontario, Canada, February 1970.

LATTICE ANISOTROPY IN ANTIFERROMAGNETIC CHROMIUM

J. A. Marcus

Professor, Department of Physics

L. H. Schwartz

Associate Professor, Department of Materials Science

E. Fawcett

Bell Telephone Laboratories

W. A. Reed

Bell Telephone Laboratories

M. O. Steinitz

Ph.D. Thesis Research (NSF Support) (Completed)

This research is jointly supported by the Advanced Research Projects Agency, the National Science Foundation and Bell Telephone Laboratories.

Objective

The objective of this investigation is to determine deviations from cubic symmetry of the lattice parameters of antiferromagnetic chromium as a function of temperature and domain orientation.

Approach

Measurements were made of the differential thermal expansion and magnetostriction of single- \bar{Q} single-crystal chromium by a three terminal capacitance technique in fields up to 100 KOe.

Progress

The project was completed with the determination of the lattice parameter ratios from the Neel temperature (312°K) to 3°K. The \bar{Q} direction was found to be the longest from 312°K to 300°K, and to be the shortest below 220°K. At the spin-flip transition from transverse to longitudinal spin-density-wave (122°K), anisotropic discontinuities in length result in a volume dilatation of 1.4×10^{-6} with decreasing temperature.

PUBLICATIONS

"Lattice Anisotropy in Antiferromagnetic Chromium," M. O. Steinitz, L. H. Schwartz, J. A. Marcus, E. Fawcett and W. A. Reed, J. Appl. Phys., 41, 1231 (1970).

MAGNETORESISTANCE OF POTASSIUM

J. A. Marcus

Professor, Department of Physics

J. E. Schaeffer

Ph.D. Thesis Research (NSF Support)

This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

The objective of this research is to determine whether the anomalous magnetoresistance observed by other investigators is due to an intrinsically non-spherical Fermi surface (Overhauser) or to spurious effects (e.g., strain) indigenous to the method of sample preparation and/or measurement.

Approach

Strain free spherical single crystals, x-ray oriented, are prepared for inductive torque measurements to study the field dependence and anisotropy of the magnetoresistance.

Progress

Measurements made on single crystals produced by a variety of methods show a non-saturating anisotropic magnetoresistance. Due to difficulties in sample orientation and handling, it is not yet clear whether these are intrinsic or secondary effects.

TEMPERATURE AND MAGNETIC FIELD DEPENDENCE OF THERMODYNAMIC PROPERTIES AT MAGNETIC PHASE TRANSITIONS

J. A. Marcus

Professor, Department of Physics

C. E. Burleson

Ph.D. Thesis Research (ARPA Support)

L. Frishman

Ph.D. Thesis Research (ARPA Support)

M. O. Steinitz

Ph.D. Thesis Research (NSF Support) (Completed)

This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

The objective of this research is to study the field and temperature dependence of thermodynamic properties in the vicinity of magnetic phase transitions.

Approach

Magnetic phase transitions will be characterized by measurements of the temperature and field dependence of the susceptibility, thermal expansion and specific heat.

Progress

Thermal expansion and anisotropy of susceptibility measurements have been made on a single crystal of alpha-uranium corroborating the existence of three transitions below 50°K. Our measurements indicate first order transitions at 23° and 37°K and a second order transition at 43°K.

PUBLICATIONS

"A Neutron Diffraction Study of the Low Temperature Chemical and Magnetic Structure of α -Mn," J. A. Oberteuffer, J. A. Marcus, L. H. Schwartz and G. P. Felcher, Phys. Rev., B2, 670 (1970).

DIRECT OBSERVATION OF LATTICE IMPERFECTIONS AND THEIR RELATION TO MECHANICAL AND PHYSICAL PROPERTIES - ELECTRON MICROSCOPIC INVESTIGATION

M. Meshii

Professor, Department of Materials Science

K. Y. Chen

Ph.D. Thesis Research (Completed)

M. T. Melluzzo

M.S. Thesis Research

M. Wada

M.S. Thesis Research

Objective

The objectives of this project are: (1) To correlate the electron microscopic structures of metals with their mechanical and physical properties; (2) To interpret the structures in the atomic scale; and (3) To establish the atomic mechanisms leading to the formation of the structures.

Approach

(1) The basic properties of lattice vacancies, such as the energies of formation, migration and interaction, are studied using electrical resistivity and electron microscopy. The magnitude of interaction among vacancies is related to the clustering of vacancies, which can be studied electron microscopically. (2) The relation between the resulting electron microscopic structure and controlling parameters, such as the degree of supersaturation, temperature (or heat treatment for vacancy reactions), alloying elements and other imperfections such as dislocations, is critically examined with theoretical calculations. (3) Having established the structure, the relation of mechanical properties to the structure will be examined. The mechanical behavior of a material of known structure is examined at various temperatures and strain rates, and a possible mechanism of strength and plastic deformation is set up to explain the observation.

Progress

Using transmission electron microscopy and electrical resistivity, the formation of vacancy clusters was studied in pure aluminum quenched into liquid nitrogen. The critical temperatures characterizing the nucleation and the growth processes were determined. A model which was consistent with the experimental results was found, with the following conclusions: (1) The C_2/C_1 ratio was small in the as-quenched state; (2) There was an initial stage which was controlled by the formation of divacancies; (3) The migration energy of divacancies and the binding

energies of di- and trivacancies are $0.4 \sim 0.5$, $0.05 \sim 0.17$ and $0.05 \sim 0.15$ eV, respectively. (4) The critical nucleus size was in the range of $7 \sim 25$ vacancy clusters. Interpretations of the colony formation and the denuded zone formation were also obtained.

Studies are in progress correlating the surface structure with the internal structure and plastic deformation behavior in quenched gold.

PUBLICATION

"Electron Microscopic Investigation of Prismatic Slip in Mg-10.5 at .% Li Single Crystals," A. Urakami, M. E. Fine, and M. Meshii, *Acta Metallurgica*, 18, 87 (1970).

INVITED TALK

"An Analysis of Solid Solution Hardening and Softening,"
Lattice Defects Symposium, Inter-University Seminar House,
Hachioji, Japan, September, 1970.

DIRECT OBSERVATION OF LATTICE IMPERFECTIONS AND THEIR RELATION TO MECHANICAL AND PHYSICAL PROPERTIES - PLASTIC DEFORMATION

M. Meshii
Professor, Department of Materials Science

J. B. Vander Sande
Ph.D. Thesis Research (Completed)

A. Novakovic
M.S. Thesis Research

D. Shetty
M.S. Thesis Research

Objective

To determine dislocation motion and dislocation multiplication during plastic deformation and to correlate these observations with macroscopic plastic deformation.

Approach

The plastic deformation is examined over a wide range of strain rate ($10^{-6} \sim 10^{-1}$) as a function of temperature, stress, and strain, by the two modes, namely, the constant stress and constant strain rate deformation. The structural information is obtained from transmission electron microscopy and surface observation. Occasionally resistivity measurements at 4.2°K are also performed. When the mobile dislocation density appears to be constant, the dislocation velocity as a function of stress can be inferred from the strain rate measurement and examined with the dislocation velocity previously determined. In specimens where the dislocation velocity is relatively well known, our investigation predicts the dislocation multiplication and the relation between the total dislocation density and the mobile dislocation density. The micro-yielding measurement and the direct measurement of dislocation velocity will be carried out by us to supplement the results.

Progress

The work hardening and the creep time law have been correlated and are being examined with possible dislocation velocity stress relations. The stress-strain relation and resistivity-strain relation were determined in detail in copper and aluminum single crystals with static and dynamic loading conditions.

The plastic deformation during the cyclic loading (fatigue condition) is being investigated with the objective of predicting the cyclic creep behavior from the static creep data.

DIRECT OBSERVATION OF LATTICE IMPERFECTIONS AND THEIR RELATION TO MECHANICAL AND PHYSICAL PROPERTIES - GOLD BASE ALLOYS

M. Meshii

Professor, Department of Materials Science

M. Graham

Ph.D. Thesis Research

This research is partially supported by the National Institutes of Health.

Objective

The objectives of this research are: (1) To examine the mechanical properties of gold and gold-base solid solutions. (2) To establish the kinetics and morphology of precipitation in gold base alloys. (3) To study the plastic behavior of the alloys at various stages of precipitation. (4) To establish the ultimate strengthening ability of this alloy system.

Approach

(1) Microhardness, resistivity and electron microscopy are employed to study the kinetics and morphology of precipitation. (2) Tensile tests and creep tests will be used to study the plasticity of single crystals of alloys whose structures are determined in (1). (3) The mechanical response of single crystals will be examined as a function of temperature, strain rate, applied stress, initial structure, and the different stages of deformation.

Progress

The precipitation-hardening study in the Au-Ti system has been completed, using polycrystalline specimens.

EFFECT OF POINT DEFECTS ON MECHANICAL PROPERTIES OF METALS

M. Meshii

Professor, Department of Materials Science

T. Mifune

Postdoctoral Research Associate (Completed)

K. Marukawa

Postdoctoral Research Associate

J. Gerard

Ph.D. Thesis Research

A. Sato

Ph.D. Thesis Research

This research is supported by the United States Atomic Energy Commission.

Objective

The purpose of this research is to investigate the role of point defects in determining the mechanical properties of metals and alloys.

Approach

Electron irradiation at low temperatures is used as a means to generate a random distribution of interstitial atoms. Using single crystals of metals and alloys as specimens, a study is made of the effects of irradiation with various doses and of the subsequent annealing on mechanical properties such as flow stress, work-hardening parameters, and the temperature and strain rate dependencies of flow stress. Interpretation of the results can be facilitated by information available on electron irradiation damage. The effects of lattice vacancies which are generated by rapid quenching are also included in the investigation. The experimental results obtained are critically examined according to the existing theories and our theoretical calculations.

Progress

The mechanical effects of self-interstitials and lattice vacancies have been characterized satisfactorily in f.c.c. metals. Theoretical calculations have been performed to examine in detail the nature of the interactions between dislocations and the atomic defects. In addition to the calculation on the misfit defect and an extended dislocation interaction, which had been reported earlier, we have performed calculations on the modulus defects and an extended dislocation interaction.

We have also applied the Peierls dislocation to the misfit defect-dislocation interaction.

The electron irradiation experiments have been performed on pure iron single crystals to investigate the rate controlling process of plastic deformation in b.c.c. metals. It has been clearly demonstrated that the presence of randomly dispersed interstitials causes a softening effect in iron. This effect can be interpreted only by the intrinsic solution softening mechanism; thus, the low temperature strength of iron must be attributed to an intrinsic property of iron such as the Peierls stress. A calculation was performed to examine the effect of misfit defects on dislocation motion in a periodic potential field. The result indicated that the mobility of dislocation can be increased (softening effect) or decreased (hardening effect) by the presence of the misfit defects, depending on temperature, applied stress and material constants such as the self-energy of dislocation, the periodic energy change and the strength of the misfit defects.

PUBLICATIONS

"Evaluation of Interactions Between a Dislocation and Imperfections Using a Continuously Distributed Dislocation Model," T. Mifune and M. Meshii, *Journal of the Physical Society of Japan*, Vol. 29, No. 3 (1970).

"Initial Hardening in Quenched Gold," M. S. Bapna, T. Mori, and M. Meshii, *Physica Status Solidi*, 40, 725 (1970).

CONTINUUM THEORY OF DISLOCATIONS

T. Mura

Professor, Department of Civil Engineering

W. Huang

Ph.D. Thesis Research

H. H. Kuo

Ph.D. Thesis Research

Objective

Theoretical prediction of inelastic behavior of materials is our final goal.

Approach

The elastic fields and the associated potential energy of the system containing dislocations are theoretically investigated by a unified method of continuously distributed dislocations which includes anisotropy of materials and dynamic states of dislocation configurations. The method is also convenient when one considers the relationship between macroscopic plasticity and dislocation theory.

The material under consideration is assumed to be an elastic continuum. The theory of elasticity is applied in the framework of linear elasticity by employing Green's tensor functions or their Fourier transforms. Any elastic field caused by imperfections in structure of materials is expressed in terms of the "equivalent" plastic distortion. The equivalent plastic distortion takes various forms according to the nature of the imperfections. Point defects, inclusions, dislocations, disclinations and phase transformations, including thermal expansions, are expressed by the equivalent plastic distortion.

Progress

The fundamental relations among dislocation density tensors, plastic distortion tensors and dislocation flux tensors are introduced by the Fourier integral method. This method is applied to find displacement and plastic distortion fields for arbitrarily given distributions of dislocations in anisotropic media. Before this result, no general method has existed for finding the displacement and plastic distortion fields caused by dislocations.

Recent work done by J. R. Willis (Phil. Mag. 21, 931, 1970) is extended to uniformly moving dislocations in anisotropic media. The

associated velocity and elastic distortion fields are obtained in explicit forms.

The displacement, stress and elastic strain energy are calculated for a circular edge disclination in an infinite elastic medium. It is pointed out that the elastic strain energy is bounded like that of a dislocation loop. The disclination loop of radius R and twist Ω has energy of order $\mu \Omega^2 R^3 \log R/r_0$, while the dislocation loop has energy of order $\mu b^2 R \log R/r_0$, where r_0 is a common inner cut-off radius. The former has a stronger R dependency than the latter.

PUBLICATIONS

"Dislocation Pile-up in Half-Space," J. G. Kuang and T. Mura, J. Appl. Phys., 40, 5017 (1969).

"A Variational Method for Limit Analysis of Anisotropic and Non-homogeneous Solids," T. Mura, S. L. Lee, and W. H. Rimawi, Developments in Theoretical and Applied Mechanics, 8, edited by D. Frederick, Pergamon Press, New York (1970).

INVITED TALKS

"Green's Tensor Functions for a Continuum with Dislocations," Systems Dynamics Seminar given for Applied Mathematics Division of the National Bureau of Standards, January 1970.

"Displacement Fields of Continuously Distributed Dislocations"

Continuum Mechanics Seminars, Princeton University, March 1970.

Engineering Materials Group Seminar, University of Maryland, March 1970.

"New Contributions to Mathematical Theory of Dislocations"

Institute of Physics, Czechoslovakian Academy of Sciences, September 1970.

The 13th Polish Mechanics Conference, September 1970.

Center of Mechanics of Solids, Rumanian Academy of Sciences, September 1970.

School of Engineering, Robert College, Istanbul, September 1970.

ANALYTICAL STUDY ON DISLOCATIONS IN THIN FILMS

T. Mura

Professor, Department of Civil Engineering

K. Saito

Postdoctoral Research Associate

S. C. Lin

Ph.D. Thesis Research

This research is primarily supported by the Atomic Energy Commission.

Objective

Stress, deformation and displacement fields caused by dislocations in thin films will be obtained by analytical methods of elasticity.

Approach

A periodic solution of stress and displacement in an infinitely extended elastic medium has been developed by us for the case when a distribution of dislocations is described by a periodic function of dislocation density tensor. This fundamental solution may be used for any arbitrary dislocation configuration, by the use of a Fourier method.

We will use the same approach in this investigation, finding the traction on the two surfaces and superimposing the opposites in order to clear the surface of the tractions. The elastic solutions will be accomplished by the method suggested by Lure. The following cases will be under consideration: A screw or edge dislocation threading a foil obliquely; a dislocation loop and a vacancy cluster; a helical dislocation; a dislocation network; and interactions between dislocations, impurities and cavities. The result will be useful for electron microscopic contrast study, stability study of distribution of dislocations, and the property of thin films as component materials in electronic and computer industries.

Progress

The state of stress and displacement in a thin film due to the presence of a periodic distribution of screw dislocations will be investigated by the method of continuously distributed dislocations and the three-dimensional theory of elasticity. The dislocations are straight and pierce obliquely the surface of the thin film. They are

distributed uniformly inside the square domains and their total strength (Burgers vector times density) inside of a square domain is constant.

Emphasis will be placed upon the stress relaxation caused by the presence of free surfaces.

DISLOCATION THEORY OF PLASTICITY

T. Mura

Professor, Department of Civil Engineering

E. A. Hudson-Phillips

Ph.D. Thesis Research

P. Wheeler

Ph.D. Thesis Research

This research is primarily supported by the National Science Foundation.

Objective

This investigation is directed towards interpreting phenomenological and mathematical formulae in classical plasticity in terms of dislocation behavior and providing new direction for the field of crystal plasticity based on a more physical background.

Approach

Stress fields in elasto-plastic materials are considered as the sum of the applied elastic stress and the dislocation stress. The Mises yield criterion is interpreted as a critical value of the Peach-Koehler force on continuous distribution of dislocations. The dislocation flux tensor is introduced and related to the plastic distortion. The constitutive equations of materials are derived from the velocity dependency of a dislocation upon the stress and the law of multiplication of dislocations.

Progress

Problems concerning wave propagation in homogeneous materials with periodically distributed eigenstrain and in composite materials were considered and parallels between the two problems investigated. It was found that, unlike the static case, no one eigenstrain problem corresponds to one composite material problem for all wave lengths. However, some interesting similarities were encountered. For example, the form of the solution for the displacements was the same in both problems. This fact is of importance in the choice of trial series for application of the Ritz energy method to the composite material problem. Using the Ritz method for laminated materials, dispersion curves can be obtained which are as close to the known exact curves as desired. Solutions can also be obtained for fiber-reinforced

materials for which there are no known exact solutions. An attempt was made, without success, to find an approximate method for obtaining dispersion curves for composite materials using solutions to geometrically similar eigenstrain problems.

MÖSSBAUER EFFECT STUDIES OF MATERIALS

L. H. Schwartz

Associate Professor, Department of Materials Science

N. Abe

Ph.D. Thesis Research

Objective

The Mössbauer effect is being used to determine the austenite fraction in steels.

Approach

Quantitative techniques will be developed by studies of Fe-Ni alloys. Fine particles of Fe-28 Ni produced chemically may be heat treated to produce samples of 100% austenite or 100% martensite. Mixtures of these two samples in various proportions produce samples of controlled austenite fraction for use as calibration of Mössbauer and x-ray diffraction austenite determinations.

Progress

Powder samples have been prepared and checked with Mössbauer spectroscopy. A sequence of controlled comparisons of the Mössbauer effect and x-ray techniques are now underway.

PUBLICATIONS

"Quantitative Analysis Using Mössbauer Effect Spectroscopy," L. H. Schwartz, Int. J. of Nondestructive Testing, 1, 353 (1970).

LATTICE ANISOTROPY IN ANTIFERROMAGNETIC CHROMIUM

L. H. Schwartz

Associate Professor, Department of Materials Science

M. Steinitz

Ph.D. Thesis Research (completed)

This research was partially supported by the Advanced Research Projects Agency and the National Science Foundation and was carried out in collaboration with Professor J. Marcus of the Northwestern University Physics Department and Drs. E. Fawcett and W. A. Reed of the Bell Telephone Laboratories.

Objective

Thermal expansion and magnetostriction measurements were made to investigate the lattice anisotropy of antiferromagnetic chromium.

Approach

Length changes were measured using a three terminal capacitance dilatometer at the low temperature facilities at the Bell Telephone Laboratories. Facilities included a 100 KG superconducting magnet.

Progress

Thermal expansion and magnetostriction measurements on single \bar{Q} , single crystal chromium gave the lattice parameter ratios in the transverse spin-density-wave phase, through the spin-flip transition, and in the longitudinal spin-density-wave phase. The spin-flip transition was found to be accompanied by anisotropic discontinuities in length resulting in a net volume dilatation of $1.4 (10)^{-6}$ with decreasing temperature. The \bar{Q} direction was found to be the longest axis at 300°K and to become the shortest axis below about 220°K. Low temperature thermal expansion yielded values for the anisotropic Gruneisen constant in marked disagreement with those obtained from low temperature magnetostriction data.

PUBLICATION

"Lattice Anisotropy in Antiferromagnetic Chromium," M. O. Steinitz, L. H. Schwartz, J. A. Marcus, E. Fawcett, and W. A. Reed, J. Appl. Phys., 41, 1231 (1970).

MAGNETIC STRUCTURE OF MnAs and MnAs_{92P08}

L. H. Schwartz

Associate Professor, Department of Materials Science

E. Hall

Ph.D. Thesis Research (Completed)

This research was supported by the National Science Foundation, and in part by the Advanced Research Projects Agency, and was carried out in collaboration with Dr. G. P. Felcher of the Argonne National Laboratory (supported by the Atomic Energy Commission).

Objective

The main objective of this research was to study the magnetic structure of MnAs in the B31 crystallographic form and examine the validity of the model proposed by Goodenough and Kafalas (Phys. Rev., 157, 389 (1967)) that the manganese is in a low spin state in the orthorhombic B31 structure, but high spin in the hexagonal B8 structure.

Approach

Powder neutron diffraction measurements have been made of MnAs at various temperatures and pressures and of MnAs_{92P08} at various temperatures.

Progress

The similarity of the ordered magnetic structures of orthorhombic MnAs (stable at high pressure) and orthorhombic MnAs_{92P08} has been confirmed using neutron diffraction. Below the magnetic ordering temperature, T_c , a canted spin structure is found for both materials. Neutron diffraction measurements from magnetically ordered and disordered temperature regions show that in these materials the Mn magnetic moment varies with the volume of the Mn atom. The variation of the magnitude of the Mn magnetic moment is explained using the relation between Pauling valence and magnetic moment introduced by Mori and Mitsui. The results are in disagreement with the currently accepted interpretation of the susceptibility data.

PUBLICATION

"Crystal and Magnetic Structure of MnAs_{92P08}," E. L. Hall, L. H. Schwartz, G. P. Felcher, and D. H. Ridgley, J. Appl. Phys., 41, 939 (1970).

STUDIES OF THE LOW TEMPERATURE DECOMPOSITION OF Fe-Cr USING THE MÖSSBAUER EFFECT

L. H. Schwartz

Associate Professor, Department of Materials Science

D. Chandra

Ph.D. Thesis Research (Completed)

This research was supported by the Inland Steel Foundation and the American Iron and Steel Institute.

Objective

The Mössbauer effect was used to investigate the decomposition of metastable iron-chromium alloys at 475°C. These experiments examined the suggestion of Lagneborg (Trans. ASM, 60, 67 (1967)) that the operating process at 475°C is spinodal decomposition.

Approach

Mössbauer effect patterns of Fe-Cr alloys were made as a function of annealing time at 475°C. Analysis of the matrix and precipitate composition were made by examining the magnitude of the magnetic hyperfine fields in the ferromagnetic matrix and iron-rich precipitate.

Progress

Mössbauer effect studies have been carried out to investigate the 475°C decomposition of binary iron-chromium alloys. Spectra of Fe-24 and Fe-60 at.pct Cr were obtained in the as quenched and annealed conditions. When the Fe-60 at.pct Cr alloy was aged at 475°C for up to 30 hours, the spectrum broadened but showed no sign of resonant absorption at energies expected for the equilibrium two phase alloy. This data is interpreted as an indication that initial decomposition produces fluctuations about the average composition, consistent with expectations for spinodal decomposition as would be predicted for this alloy at 475°C. By contrast, the Fe-24 at.pct Cr alloy lies outside the spinodal at 475°C and gives Mössbauer spectra consistent with decomposition via nucleation and growth. Limited success was achieved in attempts to synthesize the observed spectra using simple models of the hyperfine spectra and the theory of spinodal decomposition.

PUBLICATION

"Mössbauer Effect Studies of Spinodal Decomposition in Fe-Cr," D. Chandra and L. H. Schwartz, in Mössbauer Effect Methodology (ed. I. J. Gruverman), vol. 6, 1970.

INVITED TALKS

**"Mössbauer Effect Studies of Spinodal Decomposition in Fe-Cr," presented
at colloquium series of:**

International Nickel Co., Suffern, N. Y., February 1970.

Inland Steel Corporation, Whiting, Indiana, May 1970.

SULFUR DIOXIDE COMPLEXES AND SULFUR DIOXIDE -- SURFACE INTERACTIONS

D. F. Shriver

Associate Professor, Department of Chemistry

D. M. Byler

Ph.D. Thesis Research

Objective

The objective is to find structurally diagnostic vibrational spectroscopic criteria for the structures of SO_2 complexes, and to apply these criteria to a study of the surface species for adsorbed SO_2 .

Approach

Infrared and Raman data are being collected on SO_2 complexes of known structure. Ultimately the structure-spectroscopic correlations will be applied to a study of SO_2 on surfaces.

Progress

The Raman spectrum has been obtained for $\text{SbF}_5 \cdot \text{SO}_2$ in the solid state and in solution.

VIBRATIONAL STUDIES OF HALIDE COMPLEXES

D. F. Shriver

Associate Professor, Department of Chemistry

S. Leone

Undergraduate Research Participant (NSF Support) (Completed)

C. Geosling

Undergraduate Research Participant (NSF Support)

Objective

The aim of this research is to elucidate the nature of interionic forces in complex crystals.

Approach

Far-infrared and Raman studies of $[N(C_2H_5)_4]_2[InCl_5]$ and ferroelectric compounds are being undertaken.

Progress

A detailed single crystal Raman study of $[N(C_2H_5)_4]_2[InCl_5]$ has been performed. The results allow definitive assignments to be made for most of the internal modes of $InCl_5^{2-}$, which has the unexpected square pyramidal geometry. The results indicate that interionic forces are important in determining the structure of the anion. At present the pressure dependence of the infrared and Raman spectra is being studied in collaboration with Dr. J. R. Ferraro at Argonne National Laboratory. Results from these studies should enable us to gain further insight on the lattice modes and the interionic potential.

Vibrational studies are in progress on the ferroelectric compounds $[N(CH_3)_4][HgX_3]$, $X = Cl, Br, I$. Our approach involves spectroscopy on both solutions and solids. The mercury-halogen stretching modes are easily detected and assigned. As yet assignments are unclear for the metal-halogen deformation modes, which are intimately related to the ferroelectric behavior.

PUBLICATIONS

"Polarized Raman Scattering by Tetraethylammonium Pentachloroindate(III) Single Crystals. Vibrational Assignments for the Square Pyramidal $InCl_5^{2-}$ Ion," S. R. Leone, B. Swanson, and D. F. Shriver, *Inorg. Chem.*, 9, 2189 (1970).

"Vibrational Spectra, Vibrational Analysis, and Bonding in Acetonitrile--
Boron Trifluoride," B. Swanson and D. F. Shriver, Inorg. Chem.,
9, 1406 (1970).

INVITED TALK

"Single Crystal Raman Spectrum of $[(C_2H_5)_4N]_2[InCl_6]$," Illinois Institute
of Technology, Winter, 1970.

INTERACTION OF LEWIS ACIDS WITH METAL COMPLEXES

D. F. Shriver

Associate Professor, Department of Chemistry

D. Lehman

Ph.D. Thesis Research

Sr. Agnes Alich

Ph.D. Thesis Research

J. Woo

Ph.D. Thesis Research

J. Hall

Postdoctoral Research Associate (Part-time)

This research is primarily supported by the National Science Foundation.

Objective

To explore the interaction of simple Lewis acids with transition metal complexes.

Approach

Synthesis and characterization of new compounds is being performed. Characterization of these complexes is performed by chemical, spectroscopic and x-ray methods.

Progress

The formation of carbon and oxygen coordinated CO has been accomplished. This introduces a new structural feature in carbonyl chemistry. Several new compounds have been prepared from square planar metal complexes and Lewis acids.

PUBLICATIONS

"The Lewis Basicity of Metal Complexes," R. N. Scott, D. F. Shriver, and D. D. Lehman, *Inorg. Chim. Acta*, 4, 73 (1970).

"The Reaction of Trichlorostannate(II) and Trichlorogermine(II) with BF_3 " I. Wharf and D. F. Shriver, *J. Inorg. Nucl. Chem.*, 32, 1831 (1970).

"Transition Metal Basicity," D. F. Shriver, Accounts of Chem. Res.,
3, 231 (1970).

INVITED TALKS

"Carbon and Oxygen Coordinated Carbon Monoxide," Symposium on Metal-
Metal bonds, Joint ACS-CIC Meeting, Toronto, Ontario, Spring, 1970.

"Transition Metal Basicity."

McGill University, Montreal, Quebec, November 1969.

University of North Dakota, Grand Forks, North Dakota, October 1969.

Northern Illinois University, DeKalb, Illinois, March 1970.

Illinois Institute of Technology, Chicago, Illinois, 1970.

DePaul University, Chicago, Illinois, December 1969.

*Prairie View A&M, Prairie View, Texas, April 1970.

*Southwestern University, Georgetown, Texas, April 1970.

*Texas Wesleyan College, Fort Worth, Texas, April 1970.

*Robert Welch Foundation Lecturer.

METAL HYDRIDE COMPLEXES

D. F. Shriver

Associate Professor, Department of Chemistry

G. Kubas

Ph.D. Thesis Research (ARPA Supported)

A. Goya

Ph.D. Thesis Research (N.I.H. Fellow)

This research is jointly supported by the American Chemical Society Petroleum Research Fund and by the Advanced Research Projects Agency.

Objective

Our immediate goals center on the preparation and characterization of hydride bridged post-transition metal complexes. Ultimately we hope to obtain a good description of the potential energy function for M-H-M systems.

Approach

Classical chemical and spectroscopic methods are used to follow the preparation and characterization of new hydride bridged compounds.

Progress

Evidence for a double hydride bridged zinc complex has been obtained from infrared and molecular weight data. The probable structure is,



Another series of hydride containing anions with the empirical formula $\text{NaH}(\text{ZnHR})_2$ has been obtained for which NMR evidence indicates, but does not prove, the presence of hydride bridges. While the zinc hydride complexes display some novel structures and chemistry, detailed vibrational analysis is not possible because of the near coincidence of normal modes which makes assignments and band positions uncertain. Therefore we are studying group III hydrides where better separation occurs for the normal modes.

PUBLICATIONS

"The Nature of Dialkyl- and Diarylzinc Hydride Complexes," G. J. Kubas and D. F. Shriver, J. Am. Chem. Soc., 92, 1949 (1970).

"Preparation and Characterization of Alkali Metal Hydride Complexes of Bis(pentafluorophenyl)zinc. Evidence for a Double Hydride Bridge," G. J. Kubas and D. F. Shriver, Inorg. Chem., 9, 1951 (1970).

METAL POLYMER COMPLEXES

D. F. Shriver

Associate Professor, Department of Chemistry

T. Iwamoto

Associate Professor (Visiting)

This research is partly supported by a grant from the Alfred P. Sloan Foundation.

Objective

Our primary objective is to study the systematics of ethylenediamine-bridged metal complex formation.

Approach

Raman and infrared spectroscopy are being employed to distinguish bridging ethylenediamine (C_{2h} symmetry) from chelating ethylenediamine (C_2 symmetry) for a series of compounds with the formula MX_2en , where $M=Zn, Cd$ or Hg , $X=Cl, Br$ or I and en =ethylenediamine ($C_2H_8N_2$). For bridging ethylenediamine with C_{2h} symmetry the vibrational selection rules require mutual exclusion of the infrared and Raman bands, whereas coincidences are expected for chelate complexes.

Progress

Structural conclusions from the vibrational data are summarized in the table. In addition, the table shows the predicted limits of stability based on the idea that the halogen radius is a critical factor in determining the stability of the polymeric complex. The agreement is excellent.

Observed Structures For MX_2en

(P = en bridged polymer as judged by vibrational data; X = nonpolymer; * = favorable halide radius)

M \ X	Cl	Br	I
Zn	P and X	X	X
Cd	P*	P*	X
Hg	P*	P*	X

CALCULATION OF ENERGIES AND CONFIGURATIONS OF LATTICE DEFECTS IN METALS

K. S. Singwi
Professor, Department of Physics

P. V. S. Rao
Ph.D. Thesis Research

Objective

The purpose of this investigation is to calculate the energies and atomic configurations of lattice defects in simple cubic metals. Relaxation of atoms around the defect and the effects of electron redistribution will be considered.

Approach

The basic physical input into these defect calculations is the interionic potential function. Hitherto, such calculations have been made with a potential which is not very realistic. Using the self-consistent dielectric function of Singwi et. al. and the Ashcroft-type pseudopotential, Shyu, Singwi and Tosi have calculated the interionic potential in alkali metals. We have other evidence to suggest that this is a reasonable potential to use.

Progress

Using the potential of Shyu et. al., calculations of the stacking fault energies in the alkalis are in progress.

COLLECTIVE MOTIONS IN CLASSICAL LIQUIDS

K. S. Singwi

Professor, Department of Physics

K. N. Pathak

Postdoctoral Research Associate (Completed)

This research is jointly supported by the Advanced Research Projects Agency, the U. S. Atomic Energy Commission and the National Science Foundation.

Objective

Recent inelastic neutron scattering experiments and molecular dynamics computer calculations have shown that in the region of high frequency and short wave lengths, there exist collective motions in classical liquids. An interesting and basic question is: what is the nature of these collective motions? Is it possible to understand them in terms of the basic interaction between the atoms?

Approach

In the high frequency region where usual hydrodynamics is inapplicable and the microscopic structure of the liquid plays an important role, a self-consistent field method, which can be viewed as the generalization of the RPA for the electron liquid, has been used to develop a theory of collective motions. In this theory one introduces a self-consistent polarization potential that provides the restoring force and a screened response function. Various approximations for these two functions are then used.

Progress

A theory on the above mentioned lines has been developed, and has the merit that the dynamic form factors $S(q\omega)$ satisfies exactly low order moment relations. Explicit numerical calculations for the longitudinal current correlations have been made for liquid argon and the results are surprisingly in good agreement with experiments. Numerical calculations for liquid sodium are in progress.

PUBLICATIONS

"Collective Motions in Classical Liquids," K. S. Singwi, K. Sköld and M. P. Tosi, Phys. Rev. A, 454 (1970).

INVITED TALKS

**"Atomic Motions in Liquids," Colloquium at Northern Illinois University,
DeKalb, Illinois, May 1970.**

ELECTRON CORRELATIONS AT METALLIC DENSITIES

K. S. Singwi
Professor, Department of Physics

This research is jointly supported by the U. S. Atomic Energy Commission, the National Science Foundation and the Advanced Research Projects Agency.

Objective

During the last decade and a half, one of the central problems in solid state physics which has attracted considerable attention has been the study of the behavior of a degenerate electron gas at metallic densities. A very fruitful formulation of this many-body problem of an interacting electron gas is in terms of a frequency and wave number dependent dielectric function. The latter plays an important role in the calculation of many interacting metallic properties, among these are the phonon spectrum, the elastic constants, the electrical sensitivity, optical properties and properties of plasmons. It is now possible to determine these properties experimentally with fair precision-hence an ever increasing demand on a theoretician for a better dielectric function.

Approach

A very fruitful formulation of the problem of electron correlations at metallic densities (electron liquid) is in terms of a frequency and wave number dependent dielectric function. A self-consistent theory of these correlations which makes the dielectric function a functional of the Fourier transform of the pair distribution function has been developed. It has the virtue of giving a physically reasonable pair distribution function and satisfying the compressibility sum rule.

Progress

The frequency and wave number dependent dielectric function has been used to calculate a variety of interacting metallic properties, among these are the phonon spectra of alkali metals, the elastic constants, properties of plasmons and interionic potentials, with reasonable success. It has also been extended to study spin correlations in the electron liquid and has led for the first time to the calculation of the wave vector dependence of the internal magnetic field. Such a dependence is confirmed by recent experiments.

PUBLICATIONS

"Electron Correlations at Metallic Densities, III," K. S. Singwi, A. Sjolander, M. P. Tosi and R. H. Land, Solid State Communications I, 1503 (1969).

"Electron Correlations at Metallic Densities, IV," K. S. Singwi, A. Sjolander, M. P. Tosi and R. H. Land, Phys. Rev. B, 1044 (1970).

"Spin Correlations in the Electron Liquid," R. Lobo, K. S. Singwi and M. P. Tosi, Phys. Rev., 186, 470 (1969).

MANY-ELECTRON EFFECTS ON THE ENHANCEMENTS OF THE KORRINGA CONSTANT AND SPIN-LATTICE RELAXATION RATES IN ALKALI METALS

K. S. Singwi

Professor, Department of Physics

K. N. Pathak

Postdoctoral Research Associate (Completed)

P. Bhattacharyya

Ph.D. Thesis Research (ARPA Support)

This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

It is well known that the enhancements of the Korringa product and the ratio of Zeeman to dipolar spin-lattice relaxation rates in metals is due to electron-electron interaction. Recent experimental work has shown that it is not possible to explain quantitatively and understand in a consistent manner the observed spin susceptibility, the Korringa product and the relaxation rates in the alkalis.

Approach

From an analysis of previous workers in the field, it is clear that what is chiefly lacking in the theoretical treatment is the proper wave vector dependence of the effective exchange correlation potential in the generalized susceptibility expression. This effective potential has been calculated by us using the self-consistent theory of spin correlations of Singwi et al. This potential is then used to calculate the relevant quantities using the theories of Moriya and Wolff.

Progress

Numerical calculations of the Korringa constant for the alkalis and the ratio of Zeeman to dipolar relaxation times for sodium have been made and the results are in excellent agreement with experiment. This we believe to be the first satisfactory explanation of the data.

STUDIES OF HIGH TEMPERATURE MATERIALS

F. E. Stafford

Associate Professor, Department of Chemistry

J. R. Wyatt

Ph.D. Thesis Research (NIH Fellow)

G. A. Pressley, Jr.

Mass Spectrometrists

Objective

This research is directed towards the identification of the species in equilibrium with graphite, hydrogen and nitrogen at temperatures of about 2000°C, and the determination of their mechanisms of formation.

Approach

Hydrogen nitrogen mixtures, or hydrocarbons are passed through a reactor held at the temperature of interest. Material effusing from the reactor is collimated into a molecular beam. The molecular beam is intersected by an electron beam. Ions are formed and analyzed with a mass spectrometer. The neutral species originally present are deduced.

Progress

An on-line control and data gathering system was considered necessary for proper execution of these complicated experiments. The necessary interfacing was constructed, and the programs written. The system is now operating satisfactorily. The graphite-nitrogen system is being examined at about 2000°. Thermodynamic properties of some of the C-N molecules are being determined, and others, reported previously are being sought.

PUBLICATIONS

"Molecular Beam Mass Spectra and Pyrolyses of Pentaborane(9), Tetraborane Carbonyl, and Pentaborane(11): Formation and Mass Spectrum of B_4H_6 ,"
R. E. Hollins and F. E. Stafford, Inorg. Chem., 9, 877 (1970).

TRANSITION METAL OXO- AND THIO-TETRAHALIDES

F. E. Stafford

Associate Professor, Department of Chemistry

B. J. Glover

Ph.D. Thesis Research

T. F. Reynolds

Ph.D. Thesis Research

Objective

To obtain the vibrational and the electronic spectra of such molecules as MoOCl_4 and WSCl_4 in order to determine the geometry of the molecule, the electronic structure and the vibrational force constants, particularly for the deformation modes. (These molecules are 5-coordinate in the vapor but 6-coordinate in the condensed phase. We are interested in the unusual 5-coordinate species.)

Approach

Spectra in the range $40,000\text{ cm}^{-1}$ (UV) to 40 cm^{-1} (far infrared) are measured using a high temperature gas cell and a rare gas matrix isolation apparatus.

Progress

Several of the oxotetrahalides have been synthesized and their purity verified. A thiotetrahalide also has been synthesized. Measurement of the WOCl_4 spectra has started.

HIGHLY ENERGETIC SYSTEMS

F. E. Stafford

Associate Professor, Department of Chemistry

D. L. Singleton

Ph.D. Thesis Research

G. A. Pressley, Jr.

Mass Spectrometrists

This research is supported by the Atomic Energy Commission.

Objective

The objective of this program is to study high temperature species.

Approach

A mass spectrometer is used to detect species in a molecular beam effusing from either a Knudsen cell or a flow reactor.

Progress

The vapor composition above a series of transition metal dioxodihalides, oxotetrahalides and thiotetrahalides is shown to be monomeric. A correlation of these and other inorganic mass spectra is made.

PUBLICATIONS

"Mass Spectrometric Investigation of the Fragmentation Pattern and the Pyrolysis of BH_3CO ," O. Herstad, G. A. Pressley, Jr., and F. E. Stafford, J. Phys. Chem., 74, 874 (1970).

SPECTRA OF HIGH TEMPERATURE SPECIES

F. E. Stafford
Associate Professor, Department of Chemistry

M. J. Biallas
Visiting Associate Professor

K. L. Treuil
Postdoctoral Research Associate

G. Outtersen
Undergraduate Research Participant

This research is supported by the United States Army Research Office-Durham.

Objective

The main goal of this work is to obtain structural information, and from it, the thermodynamic properties of model systems and of high temperature species responsible for corrosion and mass transport of refractories.

Approach

Infrared spectra are measured with rare gas matrix isolation apparatus in the spectral range $4000-40\text{ cm}^{-1}$.

Progress

The matrix isolation apparatus is working. A glass, lightweight apparatus has been constructed. Both are being tested with transition metal compounds.

CRYSTALLOGRAPHY OF THE $\alpha \rightarrow \beta$ TRANSFORMATION OF TIN

J. T. Waber

Professor, Department of Materials Science

A. W. Ewald

Professor, Department of Physics

D. E. Pease

Ph.D. Thesis Research

Objective

The objective here is to better determine the mechanisms of the $\alpha \rightarrow \beta$ transformation in tin. That is, to examine the deformation mechanisms associated with the transformation, while at the same time looking for indications of either shear or diffusion-like behavior in the mechanism.

Approach

The basic study of the reaction will utilize a low temperature stage in the electron microscope. Samples will be transformed in the microscope, where studies of the deformation mechanisms will be carried out.

As a secondary study, single crystal samples produced in capillary tubing will be partially transformed. X-ray examination of the areas surrounding the interface will be made to search for a relationship between the two phases and the deformation of the β phase.

Progress

Large grained samples have been prepared for study using the strain anneal method. Samples suitable for study in the electron microscope have been thinned using a jet polishing technique. Preliminary studies of the slip systems in the white phase through the analysis of slip traces are currently being carried out.

A cold stage has been designed and built for the electron microscope. Initial tests have indicated that a base temperature of -73°C can be obtained when the electron beam is not on. Initial attempts to examine specimens in this unit are now in progress.

In the x-ray studies, some success has been achieved in obtaining well-formed single crystals of the α -allotrope by the capillary method. The crystals prepared by the capillary method have been transformed to the β -allotrope in a low temperature box. X-ray examination of the transformed crystals reveals considerable deformation and some polycrystalline

effects, making orientation studies difficult but some limited success has been achieved. Two orientation relations have been obtained to date:

1. $(001)_{\alpha} - (001)_{\beta} = 40^{\circ}$

2. $(001)_{\alpha} - (001)_{\beta} = 54^{\circ}$

These studies are continuing.

PITTING OF METALS

J. T. Waber

Professor, Department of Materials Science

P.V.S. Rao

Ph.D. Thesis Research

Objective

This work is directed towards determining those factors contributing to the growth of corrosion pits in metals. This work is also directed towards studying interfacial reactions in general.

Approach

A joint theoretical and experimental attack on surface reactions has continued. The experimental part has been deferred for lack of an interested student. Detailed analysis of the influence of the potential gradient near a metal surface on adsorbed atoms has been carried out using a quasi-ionic model of a metal.

Progress

A detailed paper was prepared in which the influence of the following factors on the splitting of the electronic energy levels in an adsorbable atom (or ion) was investigated:

- (1) Crystal structure of the substrate (BCC or FCC);
- (2) Nature of adsorbable atom (atomic number, bonding orbitals involved, degree of ionization);
- (3) Number of nearest neighbors associated with different crystallographic planes (hkl) bounding the solid;
- (4) Relative position of the adsorbable atom on the 2-dimensional lattice of the surface plane.

Specifically, platinum and nickel were chosen as typical FCC substrates and tungsten was chosen as a typical BCC substrate. A large collection of noble gases, atoms, metallic ions were studied. These were chosen to include both filled and incomplete p- and d-electrons. It was discovered that the crystal field splitting, ΔE , of electronic states passed through zero one or more times as the adsorbable species approached the surface from infinity. The pattern depends on the substrate and the relative position in the 2-dimensional surface lattice where the atom would strike. The lower the local symmetry of the adsorption site, the more complex the splitting pattern. The splitting ΔE was also demonstrated to increase with atomic number in a given column of the Periodic Table.

Analysis was also made of the numerical reliability of the solutions of the SCF Hartree-Fock-Slater electronic calculations. These theoretical calculations supply the quantities $\langle r^n \rangle$, the so-called expectation values of the n^{th} power of the radius and these quantities are needed to make any crystal field calculations.

POTENTIAL AND CHARGE DISTRIBUTION NEAR THE INTERFACE OF A TRANSITION METAL

J. T. Waber

Professor, Department of Materials Science

E. Kennard

Ph.D. Thesis Research (NASA Trainee)

This research is primarily supported by the National Aeronautics and Space Administration.

Objective

The objective of this research is to study the potential distribution near the surface of a heavy transition metal and to study the redistribution of electrons caused by the surface. Also, the influence of crystallographic orientation and surface defects on such potentials will be investigated.

Approach

The potentials and charge densities of free atoms are properly superimposed to form a semi-infinite solid. Body-centered and face-centered cubic and hexagonal metals will be studied.

Progress

New computer programs have permitted us to obtain contour plots of realistic crystal potentials for body-centered cubic tungsten and face-centered cubic platinum. For the first time, the potentials associated with the formation of steps and pits in a metallic surface have been calculated and shown. The potentials have been shown to deviate significantly from bulk values at one or two interatomic distances from a free surface, three or four interatomic distances from the "corners" of a surface step and one or two interatomic distances from a vacancy created in the lattice. Potentials associated with the "split" or partial vacancies which occur during the diffusion of an atom by the vacancy mechanism have also been plotted. Contour plots corresponding to the potential on the (111) and (331) faces of a platinum crystal have also been computed.

Because of the flexibility of the computer program, questions like local relaxation of atoms near a vacancy, an interstitial or a surface step can be readily investigated. This is planned for the near future.

PUBLICATIONS

"Mathematical Study of Galvanic Corrosion. Equal Coplanar Anode and Cathode with Unequal Polarization Parameters," J. T. Waber and E. Kennard, J. Electrochem. Soc., 117, 7, 880 (1970).

"SCF Relativistic Hartree-Fock Calculations on the Superheavy Elements 118-131," J. T. Waber and J. B. Mann, J. Chem. Phys., 33, 2397 (1970).

"Self Consistent Field Hartree Calculations for Atoms and Ions," J. T. Waber and A. C. Larson, Los Alamos Scientific Laboratories - LA #4297, December 1969.

INVITED TALKS

"The Quantum Chemistry of the Superactinide Elements," Robert A. Welch Foundation, commemorating the Discovery of the Periodic Table. Houston, Texas, November 1969.

"Electron Structure of Transition Elements," Colloquium, Iowa State University, Ames, Iowa, January 1970.

"Splitting of Orbitals of Ad-Atoms near a Metallic Interface," International Conference on Atomic, Molecular and Solid State Theory, Sanibel Island, Florida, January 1970.

"Potentials Near a Metallic Interface," Colloquium Talk to Quantum Theory Group, University of Waterloo, Waterloo, Ontario, Canada, February 1970.

"Superheavy Elements," Colloquium Talk, Centre European de Calcul et Moléculaire, d'Orsay, France, October 1970.

"Quantum Chemistry of Superheavy Elements," Institut of Theoretical Physik, University of Frankfurt, Main, Germany, October 1970.

THERMODYNAMICS OF SOLID, COMPOUND SEMICONDUCTORS

J. B. Wagner, Jr.

Professor, Departments of Materials Science and Engineering Science

A. V. Joshi

Ph.D. Thesis Research

N. Roessler

Ph.D. Thesis Research (NSF Trainee)

Objective

The objective is to determine the number and type of point defects in some compound semiconductors and to relate these data to mass and electron transport.

Approach

The plan of this research is to determine the dependence of the weight change and the electronic conductivity of semiconductors as a function of deviations from stoichiometry, doping additions and temperature. From gravimetric measurements, the number of defects may be inferred. From the electronic conductivity data, the type of point defects may be inferred. The chemical diffusion coefficient, and under special conditions, the self diffusion coefficient may also be obtained.

Progress

A D.C. polarization technique has been used to determine the electronic conductivity in cuprous chloride and cuprous bromide single crystals. The single crystals were grown by the Bridgman technique. The conductivity values for the single crystals were less than for polycrystalline samples. This might be due to impurities in the latter case. From the current-voltage characteristics on the samples, it was concluded that Frenkel defect model with high concentrations of defects best describe the behavior of these compounds. Further, the mobility of majority carriers in these compounds was determined from the D.C. relaxation technique as suggested by Weiss. By this method, it was concluded that the mobility of electron holes was independent of the concentration. Raleigh criticized this method and attributed the relaxation phenomenon to double layer charging at the cuprous bromide-graphite interface. The magnitude of the double layer capacitance at these interfaces is unknown. Further work is underway to determine the double layer capacitance as well as its effect on the determination of electron hole mobility in these compounds.

A Cahn microbalance and associated gas train have been set up for the determination of the redox kinetics of chromium doped manganous oxide.

PUBLICATIONS

- "Electrical Conductivity of Single Crystalline Nickel Oxide," N. G. Eror and J. B. Wagner, Phys. Stat. Sol., 35, 641 (1969).
- "The Diffusion of Mn-54 into Single Crystalline Manganous Oxide," J. B. Price and J. B. Wagner, J. Electrochem. Soc., 117, 242 (1970).
- "Chemical Diffusion in Wüstite and in Chromium-Doped Manganous Oxide," P. E. Childs and J. B. Wagner, Proceedings of the International Conference in Metallurgy and Materials Science: Heterogeneous Kinetics at Elevated Temperatures, University of Pennsylvania, September 1969, Plenum Press, pp. 269 (1970).

INVITED TALKS

- "Diffusion in Oxides," Seminar, Metallurgy Department, Iowa State University, September 1970.
- "Research Opportunities-Oxidation," Materials Symposium, Ceramics Group of the Metallurgy and Ceramics Research Laboratory, Wright-Patterson Air Force Base, Ohio, August 1970.
- "Transport in Non-Stoichiometric Crystals," Gordon Research Conference on Solid Studies in Ceramics, Meriden, New Hampshire, August 1970.
- "Mass Transport through Corrosion Product Layers," Chicago Section of Electrochemical Society, March 1970.
- "Chemical Diffusion in Non-Stoichiometric Compounds," British Ceramic Society, London, December 1969.
- "Chemical Diffusion in Oxides," Wright-Patterson Air Force Base, Ohio, January 1970.

PUBLICATIONS ON RESEARCH COMPLETED AND PREVIOUSLY REPORTED IN MRC ANNUAL TECHNICAL REPORT

- "Diffusion of Nickel into Lead Telluride Between 200 and 400°C," T. D. George and J. B. Wagner, J. Phys. Chem. Solids, 30, 2459 (1969).
- "Diffusion of Selenium-75 in Lead Chalcogenides," Y. Ban and J. B. Wagner, J. Appl. Phys., 41, 2818 (1970).

ANION DIFFUSION IN SINGLE CRYSTALS OF CoO AND NiO

J. B. Wagner, Jr.

Professor, Departments of Materials Science and Engineering Science

P. Desai

M.S. Thesis Research

This research is supported by the National Science Foundation.

Objective

The purpose of this research is to investigate the rate and mechanism of anion transport in oxides. Because of the special interest in the migration of the chloride ion through oxide layers on metals under stress corrosion conditions, the present research will be directed towards an understanding of the rate of migration of chlorine-36 into oxide crystals.

Approach

Single crystals of undoped and doped nickel and cobaltous oxides are preannealed to obtain a fixed stoichiometry. The crystals are quenched and radioactive chlorine-36 is applied to one face of the crystal. The crystal is diffusion annealed, sectioned and counted.

Progress

In preliminary runs the following tentative values are available for crystals annealed at one atm. oxygen and at 1000°C:

$$D^T (\text{Cl in NiO}) = 2 \times 10^{-12} \text{ cm}^2/\text{sec}$$

$$D^T (\text{Cl in CoO}) = 2 \text{ to } 3 \times 10^{-11} \text{ cm}^2/\text{sec}.$$

SOLUBILITY OF CARBON AND OXYGEN IN SILICON AS A FUNCTION OF TEMPERATURE

J. B. Wagner, Jr.

Professor, Departments of Materials Science and Engineering Science

T. S. Glowinke

M.S. Thesis Research

This research is supported by the International Business Machines Company.

Objective

The purpose of this work is to establish the solubility limits of carbon and oxygen separately and together as a function of temperature.

Approach

The ternary system Si-O-C at the high silicon end has been postulated by J. B. Wagner to be a ternary solid solution with decreasing solubility with decreasing temperature. The coexisting phases at moderate temperatures are postulated to be SiO_2 and SiC. A ternary phase diagram has been constructed. To test these hypotheses, wafers are equilibrated with oxygen (as SiO_2) and/or with carbon (as SiC) and then annealed. Thus, particulate matter may be precipitated following solution treatment at an elevated temperature and subsequent annealing at a lower temperature. The solubility limits are to be determined using infrared transmission and other techniques.

Progress

Single crystal wafers of silicon with known concentrations of carbon and oxygen are being annealed at various temperatures in the range 800°C-1250°C under an atmosphere of 5% H_2 -95% Ar. These samples are then etched with HF acid and the new carbon and oxygen concentrations are determined by the intensity peaks obtained in an infrared spectrum. Definite changes in the IR transmission are observed following annealing.

INVITED TALKS

"Inhomogeneities in Silicon: The Role of Carbon and Oxygen," Teletype Corporation, Skokie, Illinois, March 1970.

STUDIES CONTRIBUTING TO AN UNDERSTANDING OF THE REDUCTION OF IRON OXIDES

J. B. Wagner, Jr.

Professor, Departments of Materials Science and Engineering Science

L. Laub

Ph.D. Thesis Research

R-H. Chang

M.S. Thesis Research

This research is supported by the American Iron and Steel Institute.

Objective

The purpose of this research is to study transport in iron oxides and especially to contribute to an understanding of the role of the gas-solid reaction during reduction processes.

Approach

Thermogravimetric measurements are being used to measure the kinetics of both oxidation and reduction within the phase field of undoped wüstite. Special attention is being directed towards the characterization of the role of the surface reaction in the kinetics. Electronic conductivity measurements are being made on single crystals of $\alpha\text{-Fe}_2\text{O}_3$ as a function of oxygen pressure and temperatures.

Progress

The rate of reduction of wüstite within the phase field decreases as the concentration of oxygen in wüstite increases in agreement with previous investigations. By following the kinetics of oxidation or reduction, as the case may be, using fixed ratios of CO_2/CO and diluting this mixture with argon such that the chemical potential of oxygen was constant, the kinetics at 1062°C in an atmosphere not diluted with argon were faster than in an atmosphere diluted with 50% argon. Therefore, the process is inferred to be controlled partially by bulk diffusion and partially by a phase-boundary reaction at the wüstite-gas interface. This work on the redox kinetics of undoped wüstite has been terminated.

The D.C. electronic conductivity of single crystalline $\alpha\text{-Fe}_2\text{O}_3$ is being measured as a function of oxygen pressure and temperature. At temperatures above about 800°C the activation energy is 1.17 eV and the conductivity is independent of oxygen within the $\alpha\text{-Fe}_2\text{O}_3$ phase field. For these crystals, below 800°C , the conductivity is also independent of oxygen partial pressure but the activation energy is much lower.

PUBLICATIONS

"Chemical Diffusion in Wüstite and in Chromium-Doped Manganous Oxide,"
P. E. Childs and J. B. Wagner, *Proceedings of the International
Conference in Metallurgy and Materials Science: Heterogeneous
Kinetics at Elevated Temperatures*, University of Pennsylvania,
September 1969, Plenum Press, p. 269 (1970).

INVITED TALKS

"Chemical Diffusion in Non-Stoichiometric Compounds," *British Ceramic
Society*, London, December 1969.

SULFUR IN THE CORROSION OF SUPER ALLOYS

J. B. Wagner, Jr.

Professor, Departments of Materials Science and Engineering Science

This research is supported by the U. S. Army Office of Research-Durham.

Objective

The purpose of this research is to determine the rate and mechanism of transport of sulfur through oxides. This is one aspect of a technological problem in the hot corrosion of turbine blades.

Approach

As model systems, single crystalline NiO and CoO have been chosen. Sulfur-35 will be diffused into undoped crystals and crystals doped with aliovalent impurities.

Progress

Work has just been initiated.

INFRARED ABSORPTION STUDIES IN IMPURE INSULATORS

C. T. Walker

Associate Professor, Department of Physics

J. A. Harrington

Ph.D. Thesis Research (Completed)

Objective

The aim of this project is an understanding of the interactions between light and impurities in solids, as well as an understanding of impurity-impurity interactions. The optical selection rules for impurities in solids can differ from the phonon scattering selection rules, and thus one is able to study lattice dynamics of impurities in a way complementary to heat conductivity measurements. In addition, light absorption measurements can be made over a very broad range of impurity concentration, allowing observation of impurity-impurity interactions.

Approach

The approach is extremely straightforward. IR absorption measurements are made using the Beckman IR-9 in the Chemistry Department's Analytical Facility. We have built an optical cryostat which allows absorption studies over the range from about 7°K to room temperature. The measured spectra are then compared with spectra calculated from a theoretical model and, if necessary, one does these calculations on a computer so real crystal phonons can be employed.

Progress

In the past year we have been studying CaF_2 , SrF_2 and BaF_2 doped with H^+ and D^+ ions. This impurity, known as the U-center, is associated with an IR-active localized mode which is observed near 10μ . The IR-spectrum is quite rich, showing a fundamental, sidebands on the fundamental due to its coupling to band phonons, a second harmonic, sidebands on the second harmonic, two third harmonics and a fourth harmonic. The spectrum shifts by about $\sqrt{2}$ as one substitutes D^+ for H^+ . Most of these spectra were observed previously by others. We have gone on to study the system at very high impurity concentrations ($\sim 10^{20} - 10^{21} \text{ cm}^{-3}$) with quite interesting results. At high concentrations the fundamental and second harmonics are observed to broaden with concentration with the band width varying as the square root of the concentration. In addition, new sharp lines, not seen at low concentrations, appear at high concentrations, impurity-impurity interactions in the form of pairs, triplets, etc. of impurities. Lastly,

the sidebands on the local mode fundamental are a measure of the pure crystal phonon density of states. We have studied the density of states as a function of impurity concentration, and have observed the predicted "erosion" of the phonon critical points.

PUBLICATION

"Erosion of Phonon Critical Points in Highly Doped Crystals," James A. Harrington and Charles T. Walker, Physics Letters, 31A, 415 (1970).

INVITED TALKS

"Infrared and Raman Studies in Alkaline Earth Fluorides,"

II. Technische Hochschule, Universität Stuttgart, September 1970.

Theoretisches Teilinstitut, Universität München, September 1970.

PHONON INTERACTIONS IN INSULATING SOLIDS

C. T. Walker

Associate Professor, Department of Physics

J. A. Harrington

Ph.D. Thesis Research (Completed)

Objective

An understanding of phonon interactions in pure crystals and the interactions between phonons and impurities is the joint aim of this project. More particularly, we are interested in anharmonic effects, as seen in phonon-phonon interactions, and phonon interactions with point defects. Experimental and theoretical results from this project will assist in understanding better the properties of pure insulating solids and of insulators containing controlled impurities. In some technical applications, it is desirable for a material to be slightly impure rather than pure, but such applications rest on a fundamental understanding of the microscopic processes involved.

Approach

There are three separate activities involved in this research: (1) preparation and characterization of the materials involved, both pure and doped; (2) measurement of the temperature and concentration dependence of the low temperature thermal conductivity; and (3) analysis of experimental results in terms of models for the scattering centers, including real crystal phonon effects if appropriate.

Growth and characterization techniques employed here are standard and have been discussed in previous MRC Annual Reports. The most demanding current problem, ultra-pure NaF, is described in a separate report.

Low-temperature thermal conductivity measurements can be considered as a type of broad-band phonon spectroscopy. The temperature dependence of the thermal conductivity can be related to the frequency and temperature dependence of the phonon scattering cross-section. While the relation between these quantities is an integral over all phonon modes, one can extract reasonably detailed scattering cross-sections from the data. These are then compared with the cross-sections obtained by calculations based on some theoretical model for the scattering center. Increasingly, these theoretical calculations are done by computer since they employ the real phonon eigenfrequencies and eigenvectors obtained from inelastic neutron scattering data.

Progress

We have finished a project on CaF_2 , SrF_2 and BaF_2 doped with various impurities, such as Li^+ , Na^+ , H^+ , Sm^{++} and U^{++} . There are several remarkable features in the results. First, this broad spectrum of impurities is observed to give no resonant phonon interactions, in contrast to the experience in alkali halides. The data, in fact, seem to be explainable completely in terms of simple mass-difference scattering. Second, since the impurity scattering is apparently due to mass-difference only, it is weak. This implies that these hosts can contain significant amounts of chemical impurity ($\sim 0.1\%$) and have their thermal properties relatively unaffected. Third, the conductivity for SrF_2 and BaF_2 is significantly lower than that for CaF_2 . It is too low to be explained by background impurities and must be due to intrinsic phonon-phonon interactions in these hosts. This point merits further study

PUBLICATION

"Phonon Scattering by Point Defects in CaF_2 , SrF_2 and BaF_2 ," J. A. Harrington and C. T. Walker, Phys. Rev. B, 1, 882 (1970).

RAMAN SCATTERING IN SOLIDS

C. T. Walker

Associate Professor, Department of Physics

R. J. Harley

Postdoctoral Research Associate (ARPA Supported)

J. A. Harrington

Ph.D. Thesis Research (ARPA Supported) (Completed)

I. R. Nair

Ph.D. Thesis Research (Physics Department Fellow)

This research is supported jointly by the Army Research Office-Durham and the Advanced Research Projects Agency.

Objective

This project constitutes a third approach to the study of lattice dynamics in pure and impure crystals. From a study of Raman scattering in pure crystals, one can extract information about phonon spectra in pure crystals. The Raman effect in impure crystals provides microscopic information on impurity-lattice interactions, and is complementary to information obtained by IR or phonon spectroscopy. Thus, in practical terms, one obtains information which is useful in understanding the properties of pure and impure substances.

Approach

Raman scattering is a process in which light is scattered by a medium, with the scattered light being shifted in frequency from the incident light. The frequency shift is a direct measure of energy level spacings for the scattering center. The light source is usually a high intensity CW laser, and the scattered light is analyzed by a double-grating spectrophotometer. The polarization and direction of propagation for both the incident and scattered light, relative to the crystal axes, allow one to determine directly the symmetry properties of the scattering center. Temperature dependent studies of the spectra allow one to deduce how the scattering center is coupled to the medium. Thus, in a single experiment one obtains quite detailed microscopic information.

Progress

Three sub-projects have been studied during the past year, with substantial progress in each.

As reported last year, we have been studying Raman scattering in Tl^+ -doped alkali halides. This impurity seems to enter potassium or rubidium halides as an isotopic defect; i.e. for the even parity Raman active modes the force constants relevant for Tl appear to be the same as the pure crystal force constants. This means that the Raman spectra one observes are really phonon spectra for the pure crystal phonons. We have applied this experimental tool to the study of anharmonic interactions in KCl and RbCl, by studying the temperature dependence of the peak positions and linewidths for the various phonon peaks. We have extracted mode Gruneisen parameters, which are in good agreement with those seen by other techniques. The use of this simple, but quite precise, optical technique is just beginning.

We have continued our Raman and diffuse x-ray experiments, described last year, on KCl:KBr mixed crystals. The x-ray studies show no evidence of clustering; i.e. no evidence for Br-rich or Cl-rich regions. Thus, the observed spectra must be due to bulk properties of the mixed crystal. It appears that our most prominent Raman peaks come from two sources. One is a lattice resonance in the Cl-rich end of the concentration range, due to Br^- substituting for Cl^- . The other appears to be a zone boundary phonon at X in the Brillouin zone, whose frequency we can follow as a function of concentration. Analogous studies are underway on KBr:KI mixed crystals. This particular project has been helped substantially by the advice of Professor J. Cohen of the Materials Science Department.

The third project is Raman scattering by H^+ and D^+ in CaF_2 , SrF_2 , and BaF_2 . We have observed Raman scattering at the fundamental localized mode frequency, and by two of the second harmonics of this mode. We have also seen Raman scattering by the sidebands of the U-center fundamental, the first unambiguous observation of second order Raman scattering from impurities. Lastly, we have also seen in-band optical phonon and acoustic phonon resonances from the U-center. This is a system which has barely begun to be explored.

PUBLICATIONS

"Measurement of Anharmonic Renormalization of Phonon Frequencies,"
Richard T. Harley and Charles T. Walker, Phys. Rev. B, September 1970.

"Raman Scattering by Localized Modes," James A. Harrington, Richard T. Harley, and Charles T. Walker, Solid State Communications, 8, 407 (1970).

"Lasers: An Introduction," 16 mm color Film, produced and distributed by Coronet Instructional Films, Chicago, Illinois (1970).

SECOND SOUND IN SOLIDS

C. T. Walker

Associate Professor, Department of Physics

H. E. Jackson

Ph.D. Thesis Research (ARPA Supported)

This research is supported by the Army Research Office-Durham.

Objective

The objective of this research is observation of heat transport in insulators by thermal waves rather than by the usual diffusive mechanisms. Once observed, the temperature and frequency dependence of this phenomenon should give direct measurements of phonon-phonon scattering rates.

Approach

The experimental approach is very straightforward. One has a crystal, which is at the ultimate in purity, and evaporates a thin film heater on one side of the crystal and a thin film bolometer directly across from the heater. A pulse of electrical energy is applied to the heater and one watches the detector to see what arrives. In general one would expect to see ballistic propagation of phonons, second sound and diffusive flow of heat, depending on the temperature at which the crystal is studied.

Progress

After 3-1/2 years of effort on crystal purification we have succeeded in producing NaF crystals which are pure enough for observation of second sound. NaF was chosen because it is isotopically pure (Na and F occur in nature with one isotope each) and hence the crystal preparation problem becomes one of "merely" eliminating chemical and physical defects. By a process of crystal growth employing multiple recrystallization, we have succeeded in producing NaF crystals with purities of the order of 1 or 2 ppm. The limitation on our crystals now is dislocation densities near 10^5 cm^{-2} , which are not removed by annealing. Nevertheless, the peak thermal conductivity of these samples is about 240 watts/cm-deg, the highest value ever measured for an insulator.

In this crystal we have been able to observe propagation of second sound between 10°K and 20°K, a temperature range which agrees well with that predicted from an analysis of our thermal conductivity data. From our data it appears that the conditions on the phonon resistive scattering rate, τ_R^{-1} , relative to the non-resistive scattering rate, τ_N^{-1} , are more stringent than expected in advance. The later stages of this work were done in collaboration with the group of Professor R. O. Pohl of Cornell University, a collaboration in which we supplied the crystals and he supplied the electronics. However, we have since observed all the phenomena in our own laboratory.

With the successful observation of second sound in a conventional insulator now an accomplished fact, one can turn to the future and contemplate using the phenomenon to study phonons in other crystals.

PUBLICATIONS

"Second Sound in NaF," Howard E. Jackson, Charles T. Walker, and Thomas J. McNelly, Phys. Rev. Letters, 25, 26 (1970).

"Matter and the Molecular Theory," 16 mm color film, produced and distributed by Coronet Instructional Films, Chicago, Illinois (1970).

INVITED TALKS

"Raman Scattering and Second Sound Experiments in Alkali Halides," International Symposium on Phonons, Oberwolfach, Germany, September 1970.

"Second Sound in Solids,"

Solid State Sciences Division, Argonne National Laboratory,
November 1970.

Arizona State University, November 1970.

STUDIES OF MAGNETIC IONS IN SOLIDS

C. T. Walker

Associate Professor, Department of Physics

J. C. Gustafson

Ph.D. Thesis Research (ARPA Supported)

This research is supported by the Army Research Office-Durham.

Objective

The object of this project is quite general: the study of interactions between two or more magnetic ions and the interactions between magnetic ions and the elementary excitations in a solid, such as phonons, electrons or magnons. It is difficult to be more precise because magnetism is a broad subject and one tends to be led by the specific nature of one problem into another problem which appears, on the surface, to be totally unrelated. For example, experiments on metals and insulators would seem rather disparate, but both could be done with a view to investigating the exchange interaction.

Approach

This project employs three experimental techniques: low temperature thermal conductivity measurements, IR absorption and Raman scattering.

Low temperature thermal conductivity measurements on magnetic materials provide a means for studying many problems. In ordered magnetic systems one can study phonon-magnon interactions as well as magnon-magnetic impurity interactions. In disordered systems one studies phonon-spin and phonon-magnetic impurity interactions. But the results are complicated and one must resort to supplementary techniques to sort out the thermal information.

IR absorption and Raman scattering provide such supplementary techniques. The magnetic vector of the incident light interacts with the magnetic moment of an impurity ion or the magnetization of an ordered system, and one observes absorption or scattering. The same experimental techniques are employed here as in any absorption or scattering experiment, except that one employs an applied magnetic field as a parameter. Again, one attempts to relate his experimental data, such as peak positions and line-widths, to theoretical predictions for these observables, in order to make statements on the microscopic processes involved.

Progress

In the past year we have succeeded in growing pure (i.e. non-oxide bearing) MnF_2 , and MnF_2 doped with magnesium. Preliminary thermal conductivity experiments on these materials are in progress, and we have also taken preliminary Raman spectra. The thermal conductivity of RbMnF_3 has been measured down to $.25^\circ\text{K}$ in magnetic fields up to 45 k-Gauss. Small magnetic effects have been seen but the analysis has just begun.

PUBLICATION

"A Simple Magnetic Thermometer for Measurements Below 1°K ," John C. Gustafson, Richard T. Harley, and Charles T. Walker, Cryogenics, September 1970.

DISLOCATION THEORY

J. Weertman

Professor, Department of Materials Science

V. R. Parameswaran

Postdoctoral Research Associate

N. Urabe

Ph.D. Thesis Research

Objective

The objective of this research is to develop further the theory of dislocations, particularly moving dislocations, as applied to deformation of solids.

Approach

Use is made of dislocation theory in a linear elastic body.

Progress

Computer calculations have been made of the conditions under which subsonic edge dislocations which are smeared out on their slip planes produce zero shear stress on their slip plane. The edge dislocations are taken to move on an interface between two elastic media of differing elastic constants. If the two media have the same elastic properties, the edge dislocation must, of course, move at the Rayleigh velocity. If the elastic constants differ sufficiently there is no subsonic velocity at which a zero shear stress condition can be obtained. The dynamic friction of two elastically different materials, therefore, ought to be different, depending on whether a generalized Rayleigh velocity exists or doesn't exist for edge dislocations.

PUBLICATIONS

"A Method of Setting a Lower Limit on the Water Layer Thickness at the Bottom of an Ice Sheet from the Time Required for Upwelling of Water into a Borehole," International Symposium on Antarctic Glaciological Exploration (ISAGE), edited by A. G. Gow, C. Keeler, C. C. Langway and W. F. Weeks, Publication No. 86 of the International Association of Scientific Hydrology and the Scientific Committee on Antarctic Research, Scott Polar Research Institute, Cambridge, England, 69-73 (1970).

Book Review: Review of The Physics of Glaciers by W. S. B. Paterson, Pergamon Press, New York (1969); appeared in EOS, Transactions of the American Geophysical Union, 51, 167 (1970).

"Dislocation Motion on an Interface with Friction that is Dependent on Sliding Velocity," Ohio State University, Department of Metallurgy, Columbus, Ohio, March 1970.

HIGH SPEED DISLOCATIONS

J. Weertman

Professor, Department of Materials Science

V. R. Parameswaran

Postdoctoral Research Associate

N. Urabe

Ph.D. Thesis Research

Objective

The main goal of this research is to study the behavior of high speed dislocations in single crystals of metals.

Approach

Impact stress pulses of short duration are applied to single crystals of metals and the dislocation motion is measured from the lengths of the resulting slip bands produced on the surface or from the distance between the dislocation etch pits.

Progress

Dislocation mobility is being studied in three different BCC metals: high purity potassium, high purity iron and magnesium-lithium alloys.

Equipment has been set up to grow single crystals of potassium. A controlled atmosphere chamber has been made to handle the potassium crystals which are highly reactive in air. A few single crystals of potassium have been grown. These have to be shock loaded to study dislocation mobility.

High purity iron was obtained from Battelle Memorial Institute. The existing shock loading equipment has been modified to shock load iron. The etch pit technique will be used to study dislocation velocity in iron.

Alloys of magnesium in the BCC phase with 20, 30 and 40 wt.% Li have been obtained from the Dow Chemical Company, Midland, Michigan. A few single crystals have been grown from the 20% Li alloy. Single crystals of the higher alloys also will be grown and these will be subjected to impact stress pulses. Both the etch pit and the slip band techniques will be used to study dislocation mobility in these alloys. Indirectly, the dislocation velocity-stress exponent will be determined from the strain rate sensitivity and relaxation measurements on tensile specimens deformed by the Instron machine.

PUBLICATIONS

"Stress Dependence on the Velocity of a Dislocation Moving on a Viscously Damped Slip Plane," J. Weertman, Physics of Strength and Plasticity, edited by A. S. Argon, M.I.T. Press, Cambridge, Massachusetts, 75-83 (1969).

"Dislocation Motion on an Interface with Friction Dependent on Sliding Velocity," J. Weertman, J. Geophysical Research, 74, 6617 (1969).

INVITED TALKS

"Moving Dislocations on Slip Planes with Friction," McMaster University, Hamilton, Ontario, Canada, December 1969.

"Dislocations Moving on Fault Planes," Johns Hopkins University, Department of Earth and Planetary Science, Baltimore, Maryland, March 1970.

"Dislocation Motion on an Interface with Friction that is Dependent on Sliding Velocity," Stanford University, Stanford, California, February 1970.

"High-Speed Dislocations in Materials," V. R. Parameswaran, ASTM/IES/AIAA Space Simulation Conference, National Bureau of Standards, Gaithersburg, Maryland, September 1970.

FATIGUE OF METALS

J. Weertman

Professor, Department of Materials Science

H. Ishii

Ph.D. Thesis Research (Completed)

A. Purcell

Ph.D. Thesis Research

R. Yeske

Ph.D. Thesis Research

This research is supported by the Office of Naval Research.

Objective

This research is directed towards studying the basic mechanisms of fatigue crack propagation. The effects of the following factors are being studied: cyclic stress, static mean stress, microstructure, crystal orientation, temperature and atmosphere; to study dislocation configuration in fatigued specimens and relate these configurations to fatigue cracking phenomena.

Approach

Cu and copper alloy single crystals are used to study the effects of stacking fault energy, mean static stress and crystal orientation on the fatigue crack propagation.

Dislocation structure, fracture surface and slip band morphology around fatigue cracks are studied by transmission and replica method under the electron microscope. Thin slices of material directly ahead of the crack tip and at different distances from the tip are taken perpendicular to the sheet specimens. These slices are electropolished and observed under the electron microscope to study the changes in dislocation configuration with distance from the crack tip in a given fatigue specimen.

Progress

The fatigue experiments on pure copper and on Cu-6 wt.% Al single crystals (under cyclic loading only) have been completed at room temperature and liquid nitrogen temperature. The results are given in our ONR Technical Report No. 9, August 27, 1970.

The electron microfractography studies of the fractured specimens indicated that the fracture surface showed remarkable differences depending upon the orientation of the single crystals. Copper single crystals

oriented for easy dislocation cross slip showed the well formed striations on the fracture surface, but for crystals oriented for difficult dislocation cross slip these striations were absent. For alloy single crystals, no striations were observed in any direction. Also, specific orientation effects for sheet specimens of copper single crystals in tension-tension fatigue have been found in the earlier study; these effects have been observed for crack propagation rate and geometry.

It was deemed worthwhile to broaden the study of orientation effects by making specimens (and accompanying apparatus) amenable to: (a) sectioning in the direction perpendicular to the propagating fatigue crack tip and (b) tension-compression as well as tension-tension cyclic straining.

Preliminary preparations for tests on Cu single crystals with constant cyclic stress amplitude and variable superimposed static loading have been made. Difficulties with long-time stability of the fatigue test machine have been resolved through the use of an alternate load cylinder with good results. Vacuum annealing, x-ray orientation jigs and an improved test atmosphere control chamber have been constructed. Preliminary experiments on copper single crystals have been performed, indicating that the experimental apparatus performs as required.

PUBLICATIONS

"Fatigue Crack Propagation in Copper and Copper-Aluminum Single Crystals," H. Ishii and J. Weertman, ONR Technical Report No. 9.

"The Stress Dependence of Secondary Creep Rate at Low Stresses," J. Weertman, J. of Glaciology, 8, 54, 494 (1969).

"Creep Strength of the Earth's Mantle," J. Weertman, Rev. Geophysics and Space Sciences, 8, 1, 145 (1970).

"High Temperature Creep of Polycrystalline Graphite," W. V. Green, E. G. Zukas and J. Weertman, Mat. Sci. and Eng., 6, 3, 199 (1970).

INVITED TALKS

"A Creep Theory for Graphite Containing Microcracks," Case-Western Reserve University, Cleveland, Ohio, October 1969.

"Theory of Magma Filled Cracks and the Peach-Koehler Force on Dislocations Applied to Them," International Meeting on Mechanical Properties and Processes of the Mantle, Flagstaff, Arizona, June 1970.

MAGNETIC INTERACTIONS IN INTERMETALLIC COMPOUNDS

L. B. Welsh

Assistant Professor, Department of Physics

M. E. Johnson

M.S. Thesis Research

Objective

The general problem is to understand the magnetic interactions in various intermetallic compounds. At present we are studying the $\text{LaSn}_{3(1-x)}\text{In}_{3x}$ ($0 \leq x \leq 1$) and $\text{Co}_y\text{Ga}_{1-y}$ ($y \sim 0.5$) alloy systems.

Studies of the $\text{LaSn}_{3(1-x)}\text{In}_{3x}$ series are being done in collaboration with A. M. Toxen and R. J. Gambino at the IBM Watson Research Center. Susceptibility and specific heat measurements of these alloys indicate that although they have relatively high superconducting temperatures, the spin susceptibility may be strongly exchange enhanced. Nuclear magnetic resonance (NMR) studies are used to obtain information on the local magnetic behavior at the La and Sn sites.

In the $\text{Co}_y\text{Ga}_{1-y}$ system, the transport properties have been measured by J. O. Brittain of the Materials Science Department. His measurements indicate the presence of localized moments and the onset of magnetic ordering at $y \cong 0.56$. Our intent is to examine the magnetic properties of this system using nuclear magnetic resonance techniques. Of particular interest is the correlation of the resistance minima and negative magnetoresistance of these alloys with the nuclear magnetic resonance measurements.

Approach

The temperature and magnetic field dependence of the Knight shifts, linewidths, spin-lattice relaxation times, and spin-spin relaxation times are measured using CW or pulsed NMR techniques. The $\text{LaSn}_{3(1-x)}\text{In}_{3x}$ series is studied from 1.6°K to 300°K and the $\text{Co}_y\text{Ga}_{1-y}$ series at liquid helium temperatures.

Progress

A study of the La Knight shift and spin-lattice relaxation time in LaIn_3 appears to rule out a strongly exchange enhanced spin susceptibility as both the Knight shift and spin-lattice relaxation rate are too small and relatively temperature independent. In LaIn_3 we have concluded that the NMR experiments show no evidence for any occupation of the La d-band. The measurements are consistent with the dominance of the s-contact hyperfine interaction. In LaSn_3 a similar situation exists except that a small d-band occupation exists which modifies the temperature dependence of the La Knight shift and spin-lattice relaxation rate. The Sn NMR properties have also been measured and show no particular dependence although the Sn NMR is probably insensitive to

any p-component of the conduction electron wave function. Studies continue on other alloys in this series in an attempt to understand the origin of the large temperature dependence susceptibility of this system.

Preliminary measurements on the Co Ga_{1-y} system show a concentration dependent Knight shift of Co resonance but no concentration dependence of the Ga Knight shift. Spin-lattice relaxation time measurements indicate a very long relaxation time for the Ga NMR but a rather short relaxation time for the Co NMR of $T_1T = 0.4 \text{ sec}^\circ\text{K}$. The linewidths of the Co and Ga NMR increase considerably as $y = 0.51$ is approached, which, we believe, is due to magnetic interaction. Work on this system is continuing.

THE KONDO EFFECT IN DILUTE ALLOYS

L. B. Welsh

Assistant Professor, Department of Physics

J. Potts

Ph.D. Thesis Research

R. Redwine

Non-thesis Research (AFOSR Supported)

This research is primarily supported by the Air Force Office of Scientific Research.

Objective

The problem of interest is the nature of the Kondo state or ground state of an isolated magnetic impurity in a non-magnetic host. Of particular interest are the many-body spin-spin correlations between the magnetic impurity spin and the nearby conduction electron spins of the host. Problems under investigation concern: (1) the spatial dependence of the many-body spin-spin correlation function, (2) the time dependent fluctuations of the correlated spins, and (3) the effect of other impurities on the properties of an "isolated" impurity (i.e., impurity spin-impurity spin correlations). The alloy systems under study are very low concentrations of Fe or Cr (less than 0.1 at.%) in Cu or $\text{Cu}_{1-x}\text{Sn}_x$ alloys.

Approach

The effects of the spin-spin correlations on the Cu host conduction electron spins is determined by using the Cu nuclear spin as a probe. The Cu nuclear magnetic resonance (NMR) linewidths are used to obtain information on the dependence of the static part of the correlation function on temperature and applied magnetic field. The Cu NMR spin lattice relaxation is used to obtain information on the spin fluctuations at the Cu host site. In general it is desirable to measure these properties over a range of temperatures spanning the Kondo temperature, T_K , (30°K for CuFe, 1°K for CuCr) and magnetic fields above and below kT_K/μ_B .

Progress

Measurements on the $\text{Cu}_{1-x}\text{Sn}_x\text{Fe}$ alloy system show that the range of the static many-body spin polarization is quite small ($< \sim 50\text{\AA}$) in agreement with other recent NMR and neutron diffraction experiments and in contrast to the long-range spin polarization predicted by several theoretical treatments of the problem. Our results are consistent with an enhanced RKKY oscillating spin polarization around the impurity where the enhancement results from a localized many-body compensation of the impurity spin by the spins of nearby conduction electrons.

Preliminary measurements of the Cu spin-lattice relaxation time in CuFe indicate the spin fluctuations at the Cu site do become important but only well below T_K . The concentration and temperature dependence of the enhanced relaxation will determine whether the relaxation rates and several other observed "exotic" properties of these alloys are related to the properties of the isolated impurity or to impurity spin-impurity spin correlations.

High field (up to 75 koe) measurements of the Cu linewidths and spin-lattice relaxation time have begun but continuation of this work awaits the repair of our superconducting magnet.

THERMODYNAMICS OF ALLOYS

D. H. Whitmore

Professor, Departments of Electrical Engineering and Materials
Science

D. C. Bartosik

Ph.D. Thesis Research (Completed)

P. K. Raychaudhuri

Ph.D. Thesis Research

Objective

The primary objective of this research is to elucidate those factors which contribute to the equilibrium state of binary metallic solid solutions. Particular emphasis is placed on accurate measurements of thermodynamic properties of selected solid solutions and on the evaluation of the extent to which various factors contribute to the observed excess thermodynamic functions of these alloy systems.

Approach

Elevated temperature thermodynamic quantities for binary, metallic solid solutions are determined by employing: (1) a heated, two-chamber Knudsen effusion cell and a mass spectrometer detection instrument for activity measurements; and (2) solid-electrolyte, galvanic cell emf measurements.

Progress

Elevated temperature activity measurements involving the use of a dual-chamber Knudsen effusion cell and mass-spectrometer detection system have now been completed on a complete series of Au-Pt, Au-Pd and Ag-Pd solid solutions. In an earlier Technical Report a description of the results on Au-Pt alloys was presented and a detailed account of this work may be found in the paper listed below. The activity values for Pd and Au in Au-Pd alloys were determined mass spectrometrically at 1473°K and both sets of activity data exhibit negative deviations from ideal solution behavior for all alloys except those near the pure solvent composition. The integral excess entropy and enthalpy of these alloys are negative over the composition range investigated. To date, it has not been possible to rationalize the observed excess thermodynamic properties for this alloy system on the basis of summing estimated values for vibrational, electronic and configurational contributions to these properties.

The mass spectrometric and cell data obtained on a series of Ag-Pd alloys is remarkably self-consistent except for those alloys containing more than 80 a/o Pd, the cell data in this composition range yielding higher Ag activity values. Further experimental work using the cell technique is now underway on the high Pd alloys and a detailed analysis of the entire set of Ag activity data for these alloys will be completed in the next few months.

PUBLICATION

"Mass Spectrometric Study of the Thermodynamic Properties of Solid Au-Pt Alloys," R. W. Jones, F. E. Stafford, and D. H. Whitmore, Trans. TMS-AIME 1, 403 (1970).

DIELECTRIC AND ANELASTIC RELAXATIONS IN IONIC COMPOUNDS

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This research is supported in part by the Office of Naval Research.

Objective

The goal of this program is to observe dielectric and anelastic relaxation effects in doped ionic crystals containing point defects in order that an identification of the defect complex responsible for the relaxation and a description of its local symmetry can be made.

Approach

The linear, reversible, time-dependent response of a doped ionic crystal containing point defects to alternating electric or mechanical stress fields is followed by measuring dielectric and anelastic losses as a function of temperature and frequency. The origin of such relaxation stems from the redistribution of the defects among sites which are initially equivalent but which become inequivalent in the presence of the external field. The measured ratio of mechanical-to-electrical relaxation times is compared with theoretical predictions from many-position models to determine the local symmetry of the atomic arrangement about the point defect. E.S.R. spectra will be observed on these same doped ionic crystals to confirm the nature of the defect complex predicted by the relaxation experiments.

Progress

Dielectric losses have been observed in Mn-doped NaF crystals which have been tentatively attributed to dipoles where the Mn^{2+} ion and the Na vacancy are nearest neighbors (ground state) and next-nearest neighbors (first excited state). E.S.R. observations reported in the literature confirm the presence of these two types of dipoles in this material in comparable concentrations. Using the approach outlined by Tosi and Airoldi, which is based on the Born-Mayer theory of ionic crystals, theoretical estimates are now being made of the binding energies of the impurity-vacancy complex in both the ground and first-excited states. Equipment for the observations of ion thermal current (I.T.C.) and internal friction data has been set up, but further refinements in these experimental techniques are needed.

MASS TRANSPORT PROPERTIES OF IONIC CRYSTALS

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This research is supported by the Office of Naval Research and the Advanced Research Projects Agency.

Objective

The goal of this program is to investigate experimentally and theoretically the dominant lattice disorder of selected ionic solids, to measure tracer diffusion coefficients on pure and doped crystals of these materials and to interrelate the defect structure and the observed mass transport behavior.

Approach

The dominant lattice disorder of ionic compounds is investigated by measuring the ionic conductivity of crystals containing known concentrations of aliovalent cations. Such dopants change the concentration of lattice defects, preserve charge neutrality and chemical equilibrium, thereby allowing accurate values of the enthalpies of defect formation and defect concentrations to be obtained. Two-isotope tracer diffusion experiments on undoped crystals, conducted in both the absence and presence of an externally applied dc electric field, are employed to determine the tracer diffusion coefficient, the correlation factor and the drift mobility of the tracer species. Theoretical calculations of the formation energies of Schottky defect pairs and the binding energies for vacancy-vacancy and divalent impurity-vacancy pairs are being attempted for a variety of cubic ionic crystals.

Progress

In our Technical Report of last year, we reported on the results of applying a nonlinear least-square computer fitting technique to an extensive set of ionic conductivity data for "pure" NaF and NaF + CaF₂ crystals. Detailed information on these results and the method of analysis is provided in the publication listed below. As a result of this study, we now have satisfactory values of the defect formation and migration enthalpies and entropies for NaF and a realistic value for the enthalpy of association of cation vacancy-Ca²⁺ impurity pairs in NaF + CaF₂ crystals.

Using the modified Mott-Littleton approach proposed by Fumi and Tosi, we have recently completed a series of calculations of the Schottky pair formation energies, vacancy-vacancy pair and impurity-vacancy pair binding energies for most of the simple alkali-halide and the common divalent impurity ions. The present agreement with experiment is satisfactory and should be improved even further when account is taken in our future calculations of elastic terms and deformation dipoles.

Extensive tracer diffusion measurements, involving the diffusion of Na^{22} into NaF single crystals in the intrinsic range, indicate that there is a sizeable contribution to the observed diffusion coefficients for Na^{22} which may be attributable to the diffusion of vacancy pairs. This contribution becomes noticeable within about 100° of the melting temperature. Isotope-effect diffusion experiments, involving the diffusion of the tracers Na^{23} and Na^{24} into NaF, should be completed in the near future.

PUBLICATION

"Ionic Conductivity of Sodium Fluoride," C. F. Bauer and D. H. Whitmore, *Phys. Stat. Sol.* 37, 585 (1970).

LIQUID AND SOLID He^3

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This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

The goal of this investigation is to understand the extraordinary macroscopic properties of the condensed states of He^3 .

Approach

The standard approach of studying solid He^3 begins with a variational calculation in which the expectation value of the energy is obtained by using a cluster expansion. By exploiting the similarity between solid and liquid He^3 , we developed a partial summation of the cluster expansion which improves the convergence of the series. The partial summation carries physical implications: the crystal is visualized as properly correlated atomic clusters reacting to a uniform liquid medium. This procedure can be used to compare the structure of liquid and solid He^3 . A generalization of this approach will further solve the long-standing problem that only restricted variations are permitted in present calculations.

A natural direction of improving the variational calculation is to construct a correlated basis and perform a perturbative expansion. We are in the process of attempting this. For liquid He^3 , a similar approach led to spectacular results a few years ago.

Progress

For solid He^3 , the formulation of the problem is complete. Numerical work is in progress and awaits the availability of a large amount of computer time.

For liquid He^3 , we have on hand now a quasiparticle Hamiltonian and the Green's function formulation. Numerical work will soon begin.

PUBLICATIONS

"Quasiparticle Hamiltonian for Liquid He^3 ," H-T. Tan and C-W. Woo, J. Low Temp. Phys., 2, 187 (1970).

PHYSICAL ADSORPTION OF NOBLE GASES ON CRYSTALLINE SUBSTRATES

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Ph.D. Thesis Research (ARPA Support)

This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

This research is directed towards understanding correlation effects between adsorbed atoms, in particular, correlations which lead to condensation of monolayers, as well as understanding and predicting properties of quantum monolayers.

Approach

Beginning with a classical lattice, we compute the "external" potential seen by an adsorbed atom and solve the one-body problem. The adatom moves in a deep well in the normal direction to the crystal surface and feels the periodicity in directions parallel to the surface. Consequently, a sensible choice of basis functions consists of functions bound in the normal direction, and of Bloch-type in the plane. A perturbative calculation renders the best linear combination of these basis states. Next, a concentration of adatoms are introduced. Correlation effects become evident as concentration increases. For instance, the mobility of an adatom depends now on the competition between temperature and short-range repulsions; for fermions there is the additional competing effect of Pauli exclusion.

The interaction between a pair of adatoms arises from at least two sources: the direct interaction and interaction via phonon exchange. Direct products of the adatom wave functions described above with substrate phonon functions furnish a set of basis functions suitable for studying the strength of the phonon-induced interactions.

Progress

The first sample we look at is a helium atom adsorbed on solid argon. The choice stems from the great interest which low-temperature physicists have discovered in the experimental work performed at the University of Washington and elsewhere.

The one-body calculation is now complete. Studies on the phonon-induced interactions are underway.

PUBLICATIONS

"Communications on a Microscopic Theory of Helium Submonolayers," F. Y. Wu, H-W. Lai and C-W. Woo, J. Low Temp. Phys., 3, 332 (1970).

"Toward the Calculation of Effective Interactions in Adsorbed Helium Submonolayers," C-W. Woo, J. Low Temp. Phys., 3, 335 (1970).

"Theory of Helium Submonolayers: Formulation of the Problem and Solution in the Zero Coverage Limit," H-W. Lai, C-W. Woo and F. Y. Wu, J. Low Temp. Phys., 3, 463 (1970).

INVITED TALKS

"A Microscopic Theory of Helium Submonolayers," Seminar, University of Washington, March 1970.

PROPERTIES OF DILUTE SOLUTIONS OF He^3 IN LIQUID He^4

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This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

He^3 atoms, dissolved in liquid He^4 at very low temperatures, provide us with the best example of a Fermi liquid in nature. One finds in this system a testing ground for the quantum many-body theory. We study the correlations between experimental findings, phenomenological interpretations and microscopic theories.

Approach

A first-principle, microscopic theory of dilute He^3 - He^4 solutions begins with the construction of a set of correlated basis functions. Matrix elements, evaluated on this basis, lead to a quasiparticle Hamiltonian which contains the following information: (1) how a He^3 atom moves in the He^4 background and interacts with the phonons; (2) how it becomes dressed by the phonons and takes on an effective mass; (3) how these He^3 -quasiparticles interact with one another; (4) how the phonons become renormalized by phonon-phonon and He^3 -phonon interactions; and (5) how these effects manifest themselves in dominating the macroscopic properties of the system. All of this information may be extracted by a series of canonical transformations followed by a careful diagrammatic perturbative analysis. The results may be compared directly with experiment.

On the other hand, experimental findings too sensitive to understand quantitatively using a first-principle theory can be studied via a phenomenological theory proposed by Bardeen, Baym and Pines. The latter is qualitatively supported in all aspects by the first-principle theory mentioned earlier.

Progress

The first-principle theory mentioned above, since its completion early in 1969, has been applied to calculate various properties of He^3 - He^4 solutions. The results have been published in several stages, and have been used by all of the active low-temperature laboratories: those at Argonne, Cornell, Duke, Ohio State, etc. The agreement between theory and experiment indicates that a basic understanding of the properties of this quantum liquid solution has been achieved.

We are now engaged in studying the finer details of this problem. In particular, a controversy has of late arisen concerning the effective

interaction between a pair of He^3 quasiparticles. Combining our theory with sum rule arguments which we have recently derived, we expect to resolve this controversy within the near future.

PUBLICATIONS

"Theory of Binary Boson Solutions," W. E. Massey, C-W. Woo and H-T. Tan, Phys. Rev., A1, 519 (1970).

THEORY OF BOSE LIQUIDS AND LIQUID He⁴

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Ph.D. Thesis Research (ARPA Support)

This research is jointly supported by the Advanced Research Projects Agency and the National Science Foundation.

Objective

The aim of this project is to understand the microscopic structure of Bose liquids, in particular liquid He⁴, and to interpret and predict their macroscopic properties.

Approach

Available microscopic theories developed for treating Bose liquids include the Method of Correlated Basis Functions, sum rules and response functions, Green's functions, diagrammatic perturbation methods, and variational calculations. We, on the one hand, employ the Method of Correlated Basis Functions extensively to calculate the properties of liquid He⁴. Whenever necessary or advantageous, we combine it with the other many-body techniques listed above. On the other hand, we attempt to make clear the connections between the various techniques, toward the long term goal of unifying the quantum many-body theory.

Progress

Progress has been made in two directions: (i) correlating theoretical predictions and experimental findings concerning the properties of liquid He⁴: 3 papers have been published and one is in print; and (ii) correlating the various many-body techniques: one paper has appeared and two are in print. In (i) our interest lies in the structure of the phonon-roton spectrum of liquid He⁴, where a wealth of data have recently become available through neutron scattering, x-ray scattering and ultrasonic propagation experiments. We work closely with the experimentalists. In (ii), we have made the first connection between the highly successful method of Correlated Basis Functions and the Green's Function method.

PUBLICATIONS

"Dispersion of Phonons in Liquid He⁴," H-W. Lai, H-K. Sim and C-W. Woo, Phys. Rev., A1, 1536 (1970).

"Sum Rules, Structure Factors and Phonon Dispersion in Liquid He^4 at Long Wavelengths and Low Temperatures," D. Pines and C-W. Woo, Phys. Rev. Letters, 24, 1044 (1970).

"Diagrammatic Analysis of the Method of Correlated Basis Functions," H-K. Sim, C-W. Woo and J. R. Buchler, Phys. Rev. Letters, 24, 1094 (1970).

"Sound Velocity, Density and Gruneisen Constant in Liquid He^4 : A Comparison of Experiment with Theoretically Calculated Results," P. R. Roach, J. B. Ketterson and C-W. Woo, Phys. Rev., A2, 543 (1970).

INVITED TALKS

"The Adventures of CBF: A Microscopic Theory of Quantum Liquids," Seminar, University of Illinois, Champaign-Urbana, January 1970.

"Quantum Liquids," Colloquium, National Tsing Hua University, Taiwan, China, August 1970.

"A Microscopic Theory of Quantum Liquids," Seminar, Tokyo University of Education, Japan, September 1970.